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PREFACE

It is in those branches of natural science which border older established disciplines that the need for critical survey reviews of progress has become greatest. This has arisen partly because subjects such as geochemistry and geophysics fringe and overlap so many other fields and partly because they are at present vigorous growing points in science. A principal aim of the annual series, Chemistry and Physics of the Earth, will be to provide authoritative and up-to-date surveys of progress for those actively engaged in geophysics and geochemistry. But it is hoped also that much of what is written will encourage the interest of the chemist and physicist in a study of our planet, not merely for its own sake, but because such a study often turns out to be of benefit to physics and chemistry. Another aim is to acquaint the geologist with the results and methods of geophysics and geochemistry, particularly as progress in earth science has been hindered by some lack of liaison between different groups.

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The subject-matter coming under the heading of Chemistry and Physics of the Earth is vast and only a limited number of topics can be considered in a given volume; in general, an attempt will be made to provide a balanced variety of topics with roughly equal emphasis on chemistry and physics. Certain general topics will, however, be considered fairly regularly. Volume One contains, for example, a review of progress on the geochemistry of the halogen group of elements and other groups will be considered in subsequent years. A review of some aspects of Russian geochemistry and geophysics during the last 5 years is also given in this volume and it is hoped that such much-needed reviews can be provided from time to time.

July, 1955

L. H. Ahrens
K. Rankama
S. K. Runcorn

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1

THE ORIGIN OF THE SOLAR SYSTEM

By Sir Harold Spencer Jones

THE solar system shows so many conspicuous regularities that it could not possibly have been formed by chance. The chief characteristics of the system may be summarized as follows:

The Sun is the central and much the largest member of the system. Its diameter is about ten times that of the largest of the planets; its mass greatly exceeds the combined mass of the planets, comprising about 98·6 per cent of the total mass of the system. It has a slow axial rotation, the period of rotation being about 25 days at the equator and increasing towards the poles. Its equator is inclined to the ecliptic at a small angle.

Nine planets are known, and their orbits around the Sun are nearly coplanar. The orbital eccentricities are small, except for Mercury (0·206), the innermost, and Pluto (0·247), the outermost of the planets. The motions of revolution round the Sun are all in the same sense, which is that of the Sun's rotation. The axial rotations of the planets are also in this same sense; the obliquities of their equators to the ecliptic do not exceed 30°, except for Uranus which has the high obliquity of 98°. The masses of the four inner planets are small (the Earth being the most massive), and their mean densities are high (4·2 to 5·5 g/cm^3); the four major planets have large masses (15 to 318 times the Earth's) and their mean densities are low (0·7 to 1·6 g/cm^3). Almost all the angular momentum of the solar system is in the orbital motions of the major planets (98 per cent). Pluto appears to be more comparable with the inner planets.

Of the nine planets six have satellites: the Earth has one, Mars has two, Jupiter twelve, Saturn nine, Uranus five and Neptune two. Most of the satellites can be described as regular, in the sense that their orbits are inclined at small angles to the equator of the parent planet, that these orbits have small eccentricities and that their revolution is direct (i.e. in the same sense as the orbital motions of the planets). The outer satellites of Jupiter and Saturn and the satellites of Neptune are irregular (orbits inclined at large angles to the equators, large eccentricities and/or retrograde directions of motion).

The distances of the planets from the Sun show some degree of regularity, represented approximately by Bode's Law. This law requires a planet to exist in the gap between Mars and Jupiter. Occupying mainly this region are a large number, probably at least 30,000, of small bodies known as asteroids. Orbits have been calculated for more than 1500 of them. Many of the orbits are of high eccentricity, and some of the orbital inclinations are large. Meteorites which from time to time strike the Earth appear to be essentially similar to the smallest asteroids.

The solar system contains also a large number of comets most of which have nearly parabolic orbits, though a few of the comets with short periods have elliptic orbits. The orbit of a comet is seriously perturbed when it passes close to Jupiter. Meteor showers are associated with a number of comets, though in

some cases the comets have completely disintegrated so that they can no longer be observed.

Many theories have been proposed to account for the origin of the solar system. These theories can be divided into two groups. Those in one group are based on the assumption that the system has been formed as the result of an interaction between the Sun and another celestial body, causing a catastrophic change. These theories may be called cataclysmic and dualistic. The theories of the second group suppose that the system has been formed by the slow evolution of a primordial system. These theories may be called monistic.

Planetary systems must be much more abundant if they are formed by the slow evolution of a primordial system than if some catastrophic change is necessary to produce them. If it were possible by observation to detect planetary systems around stars and to estimate their relative frequency, a decision as to whether planetary systems have been formed mainly by the one method or by the other could be made. It is unlikely, however, that a planet of the mass of Jupiter could be detected even if associated with the nearest known star. A few of the nearer stars have been found to have companions of small mass intermediate between the mass of Jupiter and the average mass of normal dwarf stars. Such companions might be considered as either extremely massive planets or as stars of abnormally small mass.

Amongst the nearest stars about one half are known to be binary or multiple systems. It has been argued that the formation of a planetary system may be a special case of the process of the formation of binary or multiple star systems. From considerations of the mass-ratios in binary systems, KUIPER (1951) has estimated that the probability that a main-sequence star like the Sun is attended by a planetary system is of the order of 10^{-2} or 10^{-3}. If the argument is sound, all dualistic theories of the formation of the solar system must be discarded. Theories of this type, which were generally favoured until recent years, have in fact been largely superseded for other reasons by theories of the monistic type.

Two early hypotheses may be mentioned which, though they are not tenable, are not without interest today. KANT in 1755 proposed a theory according to which the Sun was supposed to have been originally at the centre of a nebula which was in rotation around the Sun under its gravitational attraction. Mutual collisions between the separate particles caused the nebula to flatten out into a disk. A gradual condensation around the denser aggregations ensued, giving rise to a number of local nebulae, each in rotation, which condensed further to give rise either to a planet or to a planet with a system of satellites. KANT supposed that the larger the planet the greater would be its gravitational attraction and the larger, therefore, would be the number of its satellites. As the rotations of the planets would be in the same sense as their revolution round the Sun while their orbital planes would be approximately in the plane of the Sun's equator, the hypothesis gave a plausible explanation of the main regularities of the solar system.

A somewhat analogous hypothesis was suggested by LAPLACE in 1796. The Sun was assumed to have been originally at the centre of a nebula, which was hot and slowly rotating. The nebula gradually cooled, condensing as it did so, the rate of rotation becoming progressively more rapid because of the conservation of the angular momentum. LAPLACE supposed that the contraction continued until the centrifugal force at the equator exceeded the gravitational pull,

when a ring of matter split off round the equator. The main mass continued to contract, several rings being thrown off in succession. Each of the rings was supposed to have aggregated into a single planet; in some of these a similar process was repeated, so giving rise to the satellite systems. The central mass eventually condensed to form the Sun. This hypothesis, like that of KANT, accounted qualitatively for the main regularities in the solar system.

But there is a fatal objection to both of these hypotheses. They are unable to account for the distribution of angular momentum in the solar system, in which, as mentioned above, the Sun has almost the whole of the mass while the major planets have almost the whole of the angular momentum. If the whole of the mass and of the angular momentum of the solar system were concentrated in the Sun, its period of rotation would be about 12 hr; but as the centrifugal force at its equator would then be only about 5 per cent of the force of gravity, rings of matter could not possibly be thrown off in the manner suggested by LAPLACE.

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If, however, the system has in the past been acted upon by outside forces, there will have been changes in its angular momentum. Various attempts have been made to formulate a scheme by which, through the interaction of an external body, the planets could have been formed and endowed with their large angular momentum. Early this century, CHAMBERLIN (1901) and MOULTON (1905) developed the planetesimal hypothesis according to which another star is supposed to have passed very close to the Sun at some remote epoch. The two bodies, moving under their mutual gravitational attraction, swung round each other in hyperbolic orbits. Near their closest approach an enormous tidal protuberance was produced on the side of the Sun facing the star which, aided by the expansion of the hot compressed solar gases, became so great that a succession of huge eruptions occurred, each accompanied by the ejection of matter. The ejected matter was pulled round by the attraction of the passing star and caused to move around the Sun in eccentric orbits, more or less in the plane of the relative motion of the two bodies.

As the ejected matter cooled, it condensed into liquid drops which quickly solidified. The denser portions are supposed to have formed the nuclei of the planets; these nuclei, as they circled round the Sun, gradually grew by accretion, sweeping up the planetesimals in their vicinity by their gravitational attraction. The residual matter formed a resisting medium, the effect of which was gradually to reduce the eccentricities of the orbits until the orbits were nearly circular. The satellites are supposed to have grown from smaller nuclei which formed close to the large planetary nuclei. This planetesimal hypothesis is purely qualitative and provides no explanation of the differences between the inner planets and the major planets.

JEFFREYS (1918) raised the objection that the planetesimals would collide with such frequency and with such high relative velocities that they would be volatilized long before accretion could have any important effect. A modified form of the theory was developed by JEFFREYS (1918) and JEANS (1917; 1919). They supposed that, at the time of the formation of the planets, the Sun was much more distended than it now is. The passage of the star near the Sun caused a long filament of matter to be drawn out from the Sun, which was unstable and broke up into a number of separate fragments, moving in elliptical orbits round the Sun. The filament would be cigar-shaped, thickest near its middle and tapering

towards its two ends, so that the largest planets would be expected to form in the middle range of planetary distances. While still only partially condensed, some of the fragments might, under suitable conditions, be broken up on their first return to the vicinity of the Sun, so producing the satellites. As in the planetesimal theory, the resistance of the residual matter is supposed gradually to have reduced the eccentricities and inclinations of the orbits to small values. Some of this matter escaped from the system but some fell back on the Sun giving it a rotation in the same direction as the orbital motion. The planets were supposed to have been set into rotation in a similar manner by matter, which had acquired momentum from the star, falling back upon them.

But the theory in this form will not stand detailed examination. JEFFREYS (1929) calculated that to account for the rotation of Jupiter the mass re-absorbed by it would have to be about one fifteenth that of the planet, or some 400 times the total mass of all its satellites, which does not seem possible. JEANS (1917; 1919) showed that the idea that the satellites were formed from the primitive planets by the tidal action of the Sun would not work.

JEFFREYS (1929) therefore revived the old idea, suggested some 200 years ago by BUFFON, that instead of a near approach of the Sun and the star there had been an actual collision. This collision was not head-on, for that would not have produced rotation, nor was it grazing, for that would not have removed enough matter, but something like a "half-ball" impact. The eruption of matter would commence before the actual impact. During the collision the heavy cores of the two bodies would swing rapidly round each other in a sharp curve. The intermingling portions of the two bodies would be greatly compressed and intensely heated, while the shearing motion would give rise to intense turbulence producing rapid rotation. As the two bodies separated, a filament of hot gaseous matter, having a rapid whirling motion, would be drawn out between them. This filament would cool by radiation and expansion and the subsequent course of events would be much as in the case of a near approach, though the rapid rotations of the major planets are accounted for.

But the theory in this form still does not solve the angular momentum difficulty. The bulk of the angular momentum in the solar system is in the orbital revolutions of the major planets and not in their axial rotations. It was assumed that, at the time of the formation of the planets, the Sun was much more distended than it now is. The assumption is no longer tenable; from the present knowledge of stellar evolution it can be inferred that the Sun must have been almost in its present state. If we suppose that the colliding star was of about the same size and mass as the Sun it was shown by RUSSELL (1935) that, on the most favourable assumptions, the angular momentum per ton of the matter from which the planets are supposed to have been formed must have been less than one-tenth of the average angular momentum per ton of the actual planetary system. The essence of the difficulty can be seen in this way: the matter from which Jupiter was formed must have been drawn out to a distance about 100 times greater than the distance between the Sun and the star at their nearest approach: the matter from which Neptune was formed must have been drawn out to about 500 times this distance. At such distances the matter would be moving nearly in a radial direction from the Sun; to obtain sufficient angular momentum the matter would need to be left moving in a direction almost at right angles to the radial direction.

In order to overcome the angular momentum difficulty, RUSSELL (1935) suggested that the Sun might originally have been a binary star and that its companion, supposed to be a good deal smaller than itself, revolved round it at a distance comparable with the distances of the present minor planets. By supposing that the intruding star collided, not with the Sun itself, but with its companion, the angular momentum difficulty is avoided, for the requisite angular momentum of the planets does not have to be produced by the collision; it is already present in the angular momentum of the orbital revolution of the companion and is merely distributed differently amongst the surviving parts of the system by the collision. The circumstances of the collision must have been such, however, that the portion of the companion which was not left behind in the form of planets, was got rid of.

LYTTLETON (1936) investigated this problem and showed that, under certain circumstances, it would be possible for both the colliding star and the Sun's companion to escape from the system, while leaving a sufficient portion of the ejected matter to revolve round the Sun under its gravitational attraction. Though the angular momentum difficulty can in this way be circumvented, it is necessary that the physical condition of the ejected matter must be such that condensation into planets is possible, and the differences between the inner and outer planets must be explained.

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NÖLCKE (1930) proved, however, that a filament of matter drawn out from the Sun would be rapidly dissipated by the action of gravitational forces, because it is inside the Roche limit, within which condensation is not possible; as the filament expands, the Roche limit, moreover, recedes.

The consideration of the physical condition of the ejected material leads to a further difficulty, pointed out by RUSSELL, which is even more serious. If the matter had been drawn out of the Sun by a near encounter with another star, its temperature must have been more than a million degrees and its pressure more than a million atmospheres; if produced by an actual collision its temperature would have been appreciably higher, probably about ten million degrees. At a million degrees the mean velocity of hydrogen atoms exceeds 100 miles a second and the attraction of the ejected mass could not prevent its rapid dissipation into space. The circumstances were investigated by SPITZER (1939) who showed that the filament, whether cylindrical in shape or in the form of a flat ribbon, would expand under its own internal pressure much more rapidly than it would lose energy either by radiation or by turbulent convection. The velocity of escape would be reached, in fact, within a few hours and the filament would then dissipate. Some of the material would escape into interstellar space; the remainder would form an extended gaseous nebula around one or more of the stars involved.

LYTTLETON (1938; 1941a, b) attempted to avoid this difficulty by supposing that the planets were formed by a two-stage process. He suggested that the first stage might have been the formation of two or more large bodies, each of sufficient size to hold together under their own gravitation. If such a body, in the course of cooling and contracting, acquires too rapid a rotation for stability, it will break up, not into a binary system nor into a planet and satellite, but into two bodies moving independently. LYTTLETON showed that the mass ratio of the two bodies so formed must be at least six to one. As the mass of Jupiter is less than six times that of Saturn, it is necessary to suppose that there must originally have been at least two bodies formed in the first stage. He further

suggests that, when instability set in, there might not have been a clean division into two separate bodies, but that secondary disturbances may have developed, so that small portions may have continued with each of the main bodies to form their satellites, while others may have become independent of them and have produced the terrestrial planets and the Moon.

The objection can be raised that the rate of rotation required for instability to occur in any of the contracting rotating masses is considerably more rapid than that of any of the planets. LYTTLETON attempted to meet this objection by the argument that the rotations of the inner planets would have been rapidly slowed down by the friction of the tides raised on them by the Sun, and that the outer planets would have progressively grown in size and mass by drawing in much of the surrounding uncondensed material through which they moved; their rotation would at the same time have been gradually slowed down, while their mean densities would have gradually decreased through the accretion of some of the surrounding material which consisted largely of the lighter elements.

As the various theories based on external disturbance from an outside star have not been able to provide a satisfactory explanation of the origin of the solar system, some theories of a catastrophic nature which do not involve such disturbance have been proposed. LYTTLETON (1938; 1941a, b) has suggested that the Sun was originally the principal components of a triple system, whose other two components were initially close together. He supposes that their masses slowly increased by accretion of interstellar matter until eventually the coalescence of the two companions was brought about. The angular momentum of the combined body was then too great for stability, so that it split into two bodies moving independently. It is conceivable that under suitable circumstances both of these bodies could have escaped from the system, leaving merely a fragment, part of the "splash" which accompanied the cataclysm, as a captive of the Sun. The planets are supposed to have been formed from this fragment. No plausible explanation is, however, provided by this hypothesis of many of the features of the solar system, for which a theory must account if it is to be considered satisfactory.

A hypothesis of a very different type has been proposed by HOYLE (1944; 1945). He supposes that the Sun was originally a member of a binary system and that its companion developed into a supernova. If the material ejected at the supernova outburst were ejected somewhat asymmetrically, as seems plausible, the binary system could have been broken up. Most of the material would have been ejected with very high velocity, because of the violence of a supernova outburst, and would have been moving much too fast to be captured by the Sun. The speed of ejection would have progressively decreased during the later stages of the outburst and sufficient material may have been captured by the Sun; the planets are supposed by HOYLE to have been formed from this material by condensation. The angular momentum requirements can be satisfied without difficulty by supposing that the separation of the two stars before the outburst was comparable with the distance of Jupiter from the Sun. This theory does not seem to be at all plausible; it is open to the same objection as those theories which suppose that material was drawn out of the Sun or out of a companion star: the matter would dissipate more rapidly than it would cool, and would form a gaseous nebula rather than a series of discrete planets.

The preceding discussion will have indicated that none of the theories of the

dualistic or catastrophic type has been able to provide a satisfactory explanation of the origin of the solar system. Some new attempts have consequently been made to account for the system on the hypothesis that it has been produced by the gradual evolution of a primordial system. Such theories all start from the assumption that the Sun was at the centre of a diffuse gaseous cloud, which may have been an interstellar cloud into which the Sun had entered, or a gaseous cloud from which the Sun had condensed or within which it had reached the last stage of its formation. The dark globules which are abundant in the Milky Way regions are believed to be "protostars", where stars are in process of condensing out of a gaseous system. The theories of this type can be divided, as ALFVÉN has pointed out, into two classes, according as they suppose the solar system to have originated through processes in which the gas was "cold" and non-ionized, or "hot" and ionized.

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ALFVÉN (1942–45; 1954) has developed a theory of the origin of the solar system of the "hot" type. He assumes that the Sun had a general magnetic field and that the gaseous cloud which surrounded it was ionized by the radiation from the Sun; the cloud was therefore electrically conducting, and ALFVÉN considers that the electromagnetic forces were of decisive importance. The essential element in ALFVÉN's theory is the part played by these forces.

The theory starts with the assumption that the Sun was at the centre of a rotating gaseous cloud, and that it was in the last phase of its formation, extending perhaps to about the present distance of Mercury. The Sun having been derived from the initial cloud, the average angular momentum of the Sun and of the cloud were of the same order and hence the angular velocity of the cloud at a distance from the Sun was considerably smaller than that of the Sun itself. The chemical constitution of the cloud may be reasonably assumed to have been generally similar to the average constitution of matter in the Universe and therefore to have consisted predominantly of hydrogen.

Such a cloud would be ionized by radiation from the Sun. The degree of ionization of any particular element will depend upon the temperature and therefore upon the distance from the Sun. In the innermost region, where the temperature is assumed to exceed 8000°K, all the elements are ionized: going outwards from the Sun, with progressively decreasing temperature, helium, hydrogen and oxygen, carbon, silicon, iron and magnesium, amongst the principal constituents, would successively cease to be ionized and would then exist only in the neutral state.

The Sun is assumed to have a general magnetic field, which must be greater than a certain critical value. The gaseous cloud tends to fall in towards the Sun under its gravitational attraction, but the magnetic field around the Sun tends to impede the fall of the ionized constituents. A gradual diffusion of the non-ionized constituents through those that are ionized consequently takes place. With increasing distance from the Sun, the degree of ionization progressively decreases and the chemical composition of the gas falling in towards the Sun therefore depends upon the distance from the Sun.

Any given constituent, in its fall towards the Sun, will sooner or later reach a distance from the Sun at which, because of its increasing temperature due in part to the conversion of gravitational kinetic energy into heat, thermal ionization sets in. The magnetic field begins to act as a brake as soon as ionization commences, and eventually stops any further fall at a distance which is roughly

proportional to the distance at which the gravitational energy is equal to the ionization energy.

ALFVÉN gives reasons for supposing that four main clouds, differing in composition, will be produced by the processes outlined. He calls these the A-, B-, C- and D-clouds. The A-cloud consists mainly of helium; the B-cloud mainly of hydrogen; the C-cloud mainly of carbon; and the D-cloud mainly of iron and silicon. There is necessarily no clear-cut separation between these clouds and each is mixed with "impurities" in the form of other elements.

As soon as the gas has become ionized, the electromagnetic forces will tend to accelerate it to the same angular velocity as the Sun. A magneto-hydrodynamic transfer of momentum from the Sun to the gas cloud takes place. This transfer of momentum is accompanied by the conversion of kinetic energy into heat, which still further increases the amount of the ionization. ALFVÉN shows that the ionization thus produced will usually be much greater than the primary ionization.

The ionized gas now moves along the magnetic lines of force towards the Sun and its motion is accelerated by gravitation. By the transfer of angular momentum to the gas a centrifugal force is produced which, if strong enough, first stops and then reverses the motion, and eventually the matter is brought along the lines of magnetic force into the equatorial plane. There is a region near the Sun within which the centrifugal force is not able to counteract gravitation. The matter within this region will fall into the Sun, that outside it is brought to the equatorial plane, where it serves as the raw material for the formation of planets. Similarly, in the case of a condensing planet, there exists a region where material is brought into its equatorial plane and is available for the formation of satellites. The demarcation between the two regions depends upon the angular velocity of the central body (Sun or planet). ALFVÉN concludes that this process leads to a rough agreement with the mass distribution found in the planetary and satellite systems; in particular, it explains why the innermost of the major planets is the largest, whereas the Galilean satellites of Jupiter are of the same size, and why the satellites of Saturn are smaller the closer they are to the planet.

The matter which has accumulated near the equatorial plane then begins to condense into small grains, which increase in size by capturing most of the molecules that collide with them. In the case of the rings of Saturn this process did not proceed very far. The material forming the rings of Saturn was unable to aggregate into a satellite because the matter is within the Roche limit, where the tidal forces produced by Saturn are larger than the gravitational force so that there is no tendency for the grains to grow by attracting surrounding matter. The existence of the asteroids is attributed to the density of the matter immediately inside Jupiter's orbit being so small that the agglomeration process could not result in the formation of a planet: ALFVÉN concludes that the asteroids have not been produced, as has often been thought, by the break-up of a planet.

In general, however, the aggregation of small grains does not lead to a stable state. The grains themselves begin to agglomerate and the bodies formed by agglomeration increase in mass with a strong tendency for more and more mass to be collected by one or two large bodies. The two processes of condensation and agglomeration are supposed to have proceeded simultaneously with a more or less continuous invasion of gas from the primary cloud.

The details of the process have been discussed by ALFVÉN at some length and

the general picture is as follows. The A-cloud, consisting of helium mixed with impurities, falls in from the region where hydrogen is also ionized, and is stopped by electromagnetic effects at about the distance of Mars. The Moon and Mars condensed out of the impurities in this cloud. The B-cloud falls in from the region where hydrogen is non-ionized, and consists mainly of hydrogen together with some helium and impurities. The A- and B-clouds may partially fall in together. The B-cloud is stopped at about half the distance of the A-cloud, and the Earth, Venus, and Mercury condense from its impurities. ALFVÉN supposes that the mass of the Sun was all the while progressively growing by accretion from the cloud; its growth displaced outwards the regions where the ionized clouds were stopped, so that the planets gathered material from a gradually increasing distance. At the beginning of the B-cloud formation, Mars and the Moon were just outside the B-cloud. In the outward displacement of the B-cloud, the Moon was captured by the Earth.

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By the time that most of the hydrogen had fallen into the Sun the ultra-violet radiation from the Sun had appreciably decreased. The first result was that carbon became de-ionized and fell in as the C-cloud, from which the four major planets were formed. At that stage, only elements with low ionization voltages were left in the initial cloud; these elements fell in as the D-cloud, consisting mainly of iron and silicon. The D-cloud was stopped outside the orbit of Neptune and only a few relatively small bodies were formed from it. Pluto was one of these bodies; the Neptune satellite, Triton, was possibly another, which was subsequently captured by Neptune.

The formation of satellites proceeded in an analogous manner from the clouds of ionized matter out of which the planets were formed. ALFVÉN shows how the main features of the satellite systems can be accounted for.

The theory is worked out in great detail and would give a plausible explanation of the main features of the solar system if the various assumptions of the theory could be accepted. A magnetic field is postulated as the agent which caused the material surrounding the Sun or planets to be suspended against gravity for long periods of time while the diffusive separation of different elements was taking place. These magnetic fields are required to exceed certain critical values, which are larger, however, than seem plausible. For the Sun the surface field that corresponds to the required dipole moment is 300,000 gauss at the present radius of the Sun, whereas the field at the present time is not more than 2 gauss. The mechanisms by which the magnetic field suspends the cloud against gravity and by which the gravitational energy, as the cloud falls in, is converted into thermal energy and into ionization are not adequately discussed. Whilst the transfer of angular momentum from the Sun to the cloud would take place by the magneto-hydrodynamic process described by ALFVÉN, there is no adequate discussion to prove that the present distribution of angular momentum, which has proved to be the stumbling block of so many theories, would in fact be brought about.

A different theory, depending upon hydrodynamical considerations, has been advanced by VON WEIZSÄCKER (1944). In contrast to ALFVÉN's theory, which assumed the cloud around the Sun to be "hot" or ionized, this theory is of the "cold" type. Like ALFVÉN's theory, the theory of WEIZSÄCKER is a modification of KANT's theory. It starts from the assumption that the Sun was at the centre of a local gas cloud, which had condensed from an eddy in the general galactic gas cloud. Collision between the various eddies in this cloud caused them to

acquire angular momentum. The solar eddy from which the planets are supposed to have condensed is assumed to have been of dimensions about the present extent of the planetary system, a mass about one-tenth of that of the Sun, and a chemical composition the same as the average cosmic composition, consisting therefore predominantly of hydrogen and helium. The Reynolds number (defined by $\rho vd/\eta$, where ρ is the mean density, v the average velocity, d a length of the order of the dimensions of the system and η the coefficient of viscosity) is very large. Using $\rho = 10^{-10}$ g/cm, $v = 10^5$ cm/sec, $d = 10$ A.U. $= 1{\cdot}5 \times 10^{14}$ cm, $\eta = 10^{-2}$ poise, it is found to be of the order of 10^{11}. Turbulence consequently developed, which considerably altered the density pattern that would be expected from gravitational theory alone. The effect of this turbulence would be to modify very appreciably the initial state, in which the atoms and dust particles in the envelope were all moving round the central body under its gravitational attraction in more or less independent orbits with their planes distributed in a more or less haphazard manner.

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Turbulence and internal frictions within the envelope changed the shape and orientations of the various particles until they were eventually reduced to orbits of nearly circular shape in the vicinity of the Sun's equatorial plane. The envelope then formed a disk whose diameter was comparable to the present diameter of the solar system and whose thickness was less than one-hundredth of its diameter. The temperature of the material at any distance from the Sun, being determined by the Sun's radiation, would then be about the same as that of a planet at the same distance. Ionization due to the solar radiation is consequently small; in the region of the major planets it is certainly absent and in the region of the inner planets it is probably absent.

The linear velocities at the outskirts of the system are likely to have been of the order of magnitude of the turbulent velocities. Viscous forces came into play, whose effect was to tend to equalize the angular velocities of the different parts of the cloud, slowing down the faster moving inner parts and speeding up the slower moving outer parts of the system. This process brings about a gradual transfer of angular momentum from the inside to the outside, and at the same time there is a dissipation of energy by the viscous forces. The matter with higher than average angular momentum, including the greater part of the lighter elements, was lost through the gradual dispersion of the envelope into outer space, while the matter with low angular momentum became concentrated towards the centre of the system. By the falling in of this matter gravitational energy was gained, which provided for the loss of mechanical energy caused by the viscous forces. The eventual state was one in which there was a slowly rotating central mass, surrounded by a faster rotating gaseous cloud, whose rotational velocities were ultimately determined by the central mass and followed KEPLER's third law. In that way WEIZSÄCKER accounts for the present distribution of angular momentum in the solar system.

But meanwhile the turbulent pattern was superposed on the Keplerian rotation. Particles of mean equal motion would collect into vortices. In order to provide a type of motion in which the vortices obstruct each other as little as possible, WEIZSÄCKER suggests that the vortices would arrange themselves into a succession of rings, giving a system of great stability, with a minimum dissipation of energy. The most stable arrangement would be attained when there is an integral number of vortices in each ring. The number assigned empirically by

WEIZSÄCKER was five, as thereby a satisfactory representation of the relative distances of Mars, the asteroids, Jupiter, Saturn and Uranus is obtained. In the neighbourhood of the circles between successive rings of vortices, there would be steep velocity gradients so that large viscous stresses would be produced and turbulence would develop. Secondary eddies, which may be regarded as in the nature of roller bearings, would form on the circles separating the main vortices, the rotation in the eddies being in the opposite direction to that in the vortices.

WEIZSÄCKER shows that the conditions for condensation will be more favourable in the roller-bearing eddies than in the vortices. The argument depends upon the mean free paths of the different particles. For the larger particles, the mean free path proves to be greater than the size of the roller-bearings, so that there will be a range of particle sizes which cannot be carried along by the roller-bearings but which can be carried along by the vortices. Condensation will therefore start in these roller-bearings; nuclei will first be formed, which will grow by accretion, as impinging particles or atoms stick to them; then, in the later stages, growth will occur by gravitational attraction when the mass exceeds a certain critical value.

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The picture is an idealized one and there would never actually be the perfect symmetry in the system of vortices. As condensation proceeded, the larger condensations would sooner or later attract the smaller and eventually the eddies in each ring would come together and form a proto-planet. It is assumed that a somewhat analogous sequence of events would follow in the atmospheres of these proto-planets and that satellite systems would be formed, but this question is not discussed in any detail. WEIZSÄCKER estimates the lifetime of the disk of matter surrounding the Sun, from which the planets condense, to be between 10^7 and 10^8 years, which is of the same order of magnitude as the period necessary to build up bodies of the size of the planets.

The theory as developed by WEIZSÄCKER is largely qualitative. Some of the details of planet formation on the basis of the theory have been discussed in a quantitative manner by TER HAAR (1948; 1950), with results of much interest. Using HEISENBERG's theory of turbulence, TER HAAR finds that the turbulent pressure in the disk will be so much greater than the gas pressure that the latter can be neglected. The optical depth in the disk is found to be small, so that the disk is fairly transparent and the energy received from the Sun at any point in it will be roughly proportional to the inverse square of the distance from the Sun. On the assumptions that the maximum planetary mass is formed at the distance of Jupiter and that the temperature at the surface of the Sun is 6000°K, the temperatures at the distances of the planets are found to decrease from 600°K at the distance of Mercury to 10°K at the distance of Neptune. It follows that ionization due to the solar radiation certainly does not occur in the region of the major planets and almost certainly does not occur in the region of the inner planets.

For condensation nuclei to form it is necessary that the vapour pressure of large particles should be less than the pressure in the gas, so that more atoms will condense on a particle than will evaporate from it. The processes involved are analogous to those involved in the formation of raindrops. The nature of the particles that will condense is determined mainly by the temperature. In the outer regions compounds like water, ammonia, carbon dioxide etc., can

condense, but in the inner regions only metals and other inorganic compounds, which are heavier and less abundant, can condense. The first stage of the condensation therefore leads to heavy bodies in the inner regions and lighter bodies in the outer, but condensation takes place much more slowly in the inner than in the outer regions. The second stage in the condensation is growth by impinging particles sticking to the nuclei, and the final stage is growth by gravitational capture. This third stage is important mainly in the case of the outer planets. The masses of the planets to be expected on this theory, assumed to be condensing at the distances of the actual planets (in terms of the mass of the Earth as unit) have been calculated by TER HAAR. The agreement between the calculated values and the actual masses of the planets is not very good, however, the calculated condensation of mass in the vicinity of the major planets being much too great.

A further difficulty is encountered when the time required for the condensation of the planets is compared with the time in which the disk would be dissipated. The time required for the condensation of the planets is of the order of 10^8 years, whereas the time required for the dissipation of the disk is computed to be only 10^3 years. TER HAAR suggests that the lifetime of the disk may have been under-estimated by a large factor, perhaps as large as 10^5, because if a regular system of vortices were established the rate of dissipation of the disk would be greatly reduced. The disk may even so have been largely dissipated, before the condensation of the outer planets had been completed, and this may account for the discordance between the computed and actual masses of the planets, referred to above.

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It is suggested that the regular satellites of the planets were already practically formed when the planets got their envelopes and that the satellite bodies were caught by these extended envelopes. Owing to the capture and subsequent loss of hydrogen, the orbits of the regular satellites were ironed out into circular orbits. The irregular satellites were probably captured at a later stage outside the envelope and consequently the ironing out of their orbits did not take place to such an extent. The regularities in the sequence of distances of the regular satellites would be expected if the satellites had been formed within regular systems of vortices. The satellites being small, gravitational capture did not play any role in their building-up process; it would therefore be expected that their densities should be higher than the densities of their primaries, but lower than the densities of the inner planets, which agrees with observation.

A question of some interest is why the outer planets have been left with a fairly rapid rotation, while the Sun has a slow rotation. The slowness of rotation of the inner planets can be ascribed to tidal friction, caused by tides raised by the Sun. The atmospheres of the outer planets would in the beginning have had angular momentum supplied to them by the large vortices, and the angular velocities in these atmospheres would correspond to KEPLER's third law; the rotational velocities of the planets would have been given by the same law. When the planetary disks started to disintegrate, the transfer of angular momentum caused the planetary rotations to slow down. The present rotational speeds correspond to a loss of about 70 per cent of the angular momentum, so that the outer planets were, in fact, appreciably slowed down before their envelopes were dissipated.

A modified form of WEIZSÄCKER's theory, in which an important role is

attributed to the process of gravitational instability, has been developed by KUIPER (1951a, b). He starts with a solar nebula surrounding the Sun with a mass about one-tenth that of the Sun, and criticizes WEIZSÄCKER's assumption that a regular system of vortices could be established and remain in existence long enough for the material from which the planets were formed to condense. KUIPER supposes that the Kolmogoroff spectrum of turbulence, derived for non-rotating media, can be applied. The distribution of eddy sizes (λ) is then given by

$$f(\lambda)d\lambda = C\lambda^{-1}d\lambda$$

where $\lambda \leq \lambda_m$, and $\lambda_m = \alpha a$, α being a numerical factor of the order of unity and a being the distance from the Sun. The above formula means that the distribution in log λ is independent of λ. Large eddies, up to the maximum size, may be found anywhere in the nebula, and the distribution will show no preferential correlation with distances to the Sun. Small eddies may be found inside larger eddies as well as outside them. These eddies are continually forming and dissolving, the largest eddies deriving their energy from differential Kepler motions around the Sun, and the smaller ones deriving theirs from the larger ones. The largest eddies have the longest lives. KUIPER shows that the "roller-bearing" eddies, which may form when primary eddies collide, would be of higher temperature but only slightly higher densities than the primary eddies and that they would be short-lived. Even the large eddies prove to have comparatively short lifetimes, of the order of 100 years. The repeated formation and dissolution of these eddies could not produce the small number of large condensations, as supposed by WEIZSÄCKER, but would give rise to innumerable small ones.

There is no escape from this result unless gravitational action can keep some of the large vortices together long enough for massive condensations to form; for that to be possible their densities must exceed the critical value at which the internal attractions within the cloud and the solar tidal force are equal, for otherwise disruption by tidal action will ensue. This critical density, called the Roche density, varies inversely as the cube of the distance from the Sun, or inversely as the square of the period of revolution round the Sun. KUIPER concludes that the segregation of planetary masses took place essentially at the Roche density. If Δ denotes the distance between the centres of two masses whose mean distance from the Sun is a, KUIPER concludes that the planetary masses under these circumstances should be proportional to $(\Delta/a)^3$, a result which he finds is approximately satisfied by the actual planetary masses and distances. The satellite systems are found also to satisfy the same empirical relationship.

KUIPER concludes that the flattening of the solar nebula towards its plane of symmetry would be much greater than estimated by WEIZSÄCKER and TER HAAR; they assumed that the component of the force of gravity at right angles to this plane was almost entirely due to the solar attraction, whereas in KUIPER's development of the theory the attraction of the nebula itself is predominant. In consequence an increase in flattening by a factor of about 25 results, with a correspondingly large increase in density, which permits gravitational instability to become operative. The initial density fluctuations caused by turbulence will be amplified by the action of gravitational instability so that large clouds, the proto-planets, are formed, which are gravitationally stable. They therefore exist

long enough for condensation processes to develop and for large masses to be formed instead of a very great number of small masses. On the assumptions that the proto-planets grew until they touched their neighbours on each side and that the planets were formed at their present distances from the Sun, the diameters of the proto-planets at their maximum extent and their masses are deduced. When these masses are plotted against the present planetary masses, the points are found to lie very closely on a smooth curve.

From this result KUIPER draws two conclusions. In the first place the distances of the planets from the Sun can not have changed greatly since their formation, at least not in an irregular manner, otherwise such a close relationship could not have been preserved. Secondly, the differences between the masses of the planets are not attributable to the distances from the Sun at which they were formed; e.g. the Earth is less massive than Jupiter not because it originated closer to the Sun but because proto-Earth was less massive than proto-Jupiter. The existence of the small planet Pluto beyond the major planets consequently presents no difficulty. KUIPER finds that the mass of the part of the solar nebula that formed the proto-planets was about 0·06 that of the Sun, so that a reasonable value for the total mass of the nebula is 0·1 that of the Sun.

KUIPER concludes that the so-called Bode's Law is not a real law but is a consequence of the density distribution in the original solar nebula. The larger the density in terms of the local Roche density, the larger the ratio between the radii of two consecutive orbits and the larger the masses of the planets. If the density of the solar nebula had been less by a factor of 2 or 3, planets would not have formed but a large number of small masses would have resulted. If the density had been larger by a factor of 2 or 3, no ordinary planets would have formed but one or more stellar companions would have been produced. The ratio of the surface density of the nebula to the local Roche density determines what sort of system will evolve.

By this theory the common direction of revolution of the planets is accounted for; their small orbital inclinations are the result of the flatness of the solar nebula; the nearly circular orbits are a consequence of the internal viscosity of the nebula. The direct rotation of the planets is produced by solar tidal friction on the proto-planets. Even though the initial rotation was in the opposite direction, a forced rotation, with a period equal to the orbital period, would soon be imposed on the proto-planets. As they contracted their angular velocity tended to increase, while the solar tides tended to maintain synchronization. As the density increased, the effect of the solar tides gradually decreased and eventually the rotation became more rapid than the revolution period. The angular momentum per unit mass of the present planets is much smaller than the initial angular momentum per unit mass of the proto-planets, as much angular momentum was lost by the escape of gases from the periphery as the proto-planets contracted. The present periods of rotation of the planets can not be accounted for quantitatively, however.

The regular satellites are supposed to have been formed in a manner analogous to that by which the planets themselves were formed. The irregular (retrograde) satellites of Jupiter and Saturn are attributed to glancing collisions between the corresponding proto-planets; the regions in contact could acquire retrograde motion and the irregular satellites are supposed to have been formed from these regions of retrograde motion. If such a mechanism is correct, retrograde

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satellites are to be expected only in the outer region of a satellite system and such satellites could be preserved only if the proto-planet did not subsequently lose a large part of its mass. An alternative possible origin for the irregular satellites is that they were released in the early stages of proto-planet contraction and were subsequently recaptured; in that case either direct or retrograde orbits would be possible. There is no mechanism, on either hypothesis, by which practically circular orbits can be attained for the irregular satellites.

The outermost region of the solar nebula (beyond proto-Neptune) had a surface density below the limit at which stable proto-planets could be formed. Condensation products, of substances such as water, ammonia, methane etc., in the solid or frozen state must have formed in that region because of the low temperature. These would have slowly collected to form larger aggregates. KUIPER suggests that these aggregates were the comets and that they were scattered through the solar system by the perturbing action of Pluto.

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KUIPER's theory has been based on the assumption that the Sun was already formed as a star, with a size and luminosity much as at present, before the proto-planets were formed. The theory would be equally valid, however, if the Sun had not altogether completed its contraction and if its radius at the time the planets were formed was several times greater than at present. No explanation is provided by the theory for the slow solar rotation, which KUIPER thinks may have to be sought in the general problem of why almost all G-type dwarf stars have slow rotations. On this monistic type of theory of the origin of the solar system, an explanation of the slow rotation of the Sun is not so essential as it is on any type of dualistic theory in which the distribution of angular momentum between Sun and planets has to be accounted for by the action of an extraneous body.

Several details of KUIPER's theory have been criticized by TER HAAR (1953). He considers that the gaseous disk would not be flattened towards its equatorial plane to the extent asserted by KUIPER for two reasons. The gravitational field of the Sun can not be neglected in comparison with the gravitational force due to the disk itself: the Sun's field might be comparable with or possibly even greater than the field due to the disk. Secondly, KUIPER used the thermal velocity instead of the turbulent velocity in his derivation of the height of the disk. TER HAAR's estimate of the height of the disk is forty times greater than KUIPER's. In consequence the densities required by KUIPER's theory of the formation of the planets would not be attained. The conclusion reached by TER HAAR is that it may not be possible to account satisfactorily for the origin of the solar system by processes taking place after the Sun has reached its present state and in that event a theory is required that will account at the same time for the formation of the Sun and for the formation of the planetary system. The difficult problem of accounting for the slow rotation of the Sun will then again be met.

The problem of formulating a satisfactory theory of the origin of the solar system is therefore still not solved. Some important advances have been made in recent years and it now seems that a monistic theory is much more likely to succeed than a dualistic theory. Some modifications of one or other of the monistic theories or a suitable combination of them may perhaps in due course lead to a theory that is free from objections.

The investigations of UREY (1951; 1952) concerning the mode of formation

of the planets have not been mentioned in this review of theories of the origin of the solar system. UREY's work is not concerned with the actual origin of the solar system; it consists of a detailed discussion, based to a large extent upon chemical considerations, of the way in which the Earth, Moon and terrestrial planets could have been formed from a cloud of gas, dust particles and planetesimals. Investigations of this type are required to supplement any theory of the origin of the solar system which succeeds in explaining how matter has been brought into close proximity with the ecliptic plane and in suitable amounts at the proper distances from the Sun to form the planets and their satellite systems as we find them today. UREY's work is of great interest and is deserving of careful study; it is an important contribution to the study of how the planets might have developed from the proto-planets.

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TEMPERATURES WITHIN THE EARTH

By J. VERHOOGEN

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NOTATION

T = temperature; P = pressure; V = volume; S = entropy
t = time
a, b, c = constants
c_P = specific heat at constant pressure, c_V = specific heat at constant volume
r = distance from the centre of the earth
R = radius of the earth
x = depth, counted from the surface
ρ = density
α = coefficient of thermal expansion $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$
(also internal pressure, in SIMON's theory of melting, p. 27).
k = Boltzmann's constant; R = gas constant; N = Avogadro's number R/k
k = thermal conductivity (cal/cm deg sec)
h^2 = thermal diffusivity (cm²/sec)
K_T = isothermal incompressibility $= \rho\left(\frac{\partial P}{\partial \rho}\right)_T$
K_S = adiabatic incompressibility $= \rho\left(\frac{\partial P}{\partial \rho}\right)_S$
v_p = velocity of longitudinal elastic waves
v_s = velocity of transverse elastic wave
ε = rate of heat generation (cal/cm³ sec), also activation energy per particle
q = heat flow (cal/cm² sec)
σ = electrical conductivity
β = temperature gradient
g = acceleration of gravity

THE closely related problems of temperature distribution and distribution of heat sources within the earth are of fundamental importance in all speculations regarding the earth's constitution and behaviour; there is hardly a chapter of geology or geophysics that is not concerned with them. Indeed, all properties of earth matter at any depth (e.g. viscosity, elasticity, strength, electrical conductivity, etc.) are determined in part, and sometimes in a large part, by the temperature prevailing at that depth. To the geologist, whose concern is to find a plausible explanation and mechanism for such phenomena as deformation, mountain making, or igneous activity, there is little doubt that the ultimate source of energy involved is thermal; what happens at the surface depends on what heat sources are available and where. Of all observable geological phenomena, the surface heat flow is, energy-wise, the most impressive, as the energy output per unit time for the whole earth (ca. $6{\cdot}5\ 10^{27}$ ergs/year) is about 10 to 100 times larger than the total energy involved in earthquakes or volcanic activity. Even the greatest geological cataclysm is, in terms of the energy involved per unit

time, a second-order phenomenon. No astrophysicist would bother to develop a physical theory of the sun only to explain sunspots, neglecting its main energy output. In the same sense geophysicists must first attempt to develop a model of the earth that will account for its main heat output. It may be hoped that when this is done second order effects such as geological phenomena will take care of themselves.

The temperature distribution within the earth is, of course, essentially determined by the intensity and distribution of heat sources of which the most important are radioactive matter and, possibly, residual heat if the earth initially formed at high temperature. We may have to add to this list gravitational potential energy resulting from a redistribution of masses inside the earth (UREY 1952). If these sources were exactly known as to their position and strength, the temperature distribution would automatically follow. Alternatively, one may attempt to determine the temperature and infer from this datum the distribution of heat sources. Methods used may be roughly classified as follows:

1. Methods using as primary datum the surface heat flow, and additional hypotheses regarding the distribution of radioactive matter.
2. Methods based on melting-point relationships.
3. Methods based on seismic data and solid-state theory.
4. Methods based on electrical and magnetic phenomena.

These methods may be further subdivided according as heat transfer is assumed to take place mainly by (*a*) conduction or (*b*) convection. The former are the most common and, historically, the most important.

CONDUCTIVE HEAT TRANSFER
THE THERMAL HISTORY OF THE EARTH

The procedure, in broad outline, is as follows. Assume that conductive heat transfer becomes important at a certain time, say t_0 years ago, which we take as the origin of time. This initial moment would coincide either with the formation of the earth, if it formed in the cold state, or with solidification, if it formed from the liquid state. Assume an initial temperature distribution $T_0 = f(r)$, where r is the distance from the centre of the earth. Assume further a certain distribution of radioactive matter corresponding to a heat generation ε cal/cm^3 sec.; ε is a function of t and r. The equation of heat conduction for spherical symmetry is

$$\rho c_P \frac{\partial T}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(kr^2\frac{\partial T}{\partial r}\right) + \varepsilon(r, t). \qquad \ldots.(1)$$

The boundary conditions are:

$$\text{for } t = 0\text{: } T_0 = f(r)$$

$$\text{for } t = t_0\text{: } k\left(\frac{\partial T}{\partial r}\right)_{r=R} = q_R$$

where q_R is the surface heat flow at the present time. In addition we set $T = 0$ for $r = R$ and $\left(\frac{\partial T}{\partial r}\right)_{r=0} = 0$ for all t's. We note that ρ, c and k are functions of pressure, temperature and composition; hence they are also functions of r and t.

A complete and exact solution of this equation has not been achieved as yet. It would require a knowledge of t_0, the age of the earth, of the distribution function $\varepsilon(rt)$, of the variation of k, ρ, c with depth and temperature, and of the initial temperature distribution T_0. None of this information is directly available and additional assumptions must be made. A common assumption is that $h^2 = k/\rho c$ remains constant within the earth or part of it.

Holmes' Solution

All work done prior to the discovery of radioactivity, and of its importance in the thermal history of the earth (RAYLEIGH, 1906), is now only of historical interest. HOLMES (1915; 1916) in 1915 was the first to make quantitative use of the (then) recently measured values of heat generation by radioactive decay in rocks. He adopted the (then) generally accepted value $t_0 = 1{\cdot}6$ billion years (1 billion $= 10^9$), and set ε independent of time. He further assumed that radioactivity decreases with depth x according to an exponential law $\varepsilon = \varepsilon_0 e^{-ax}$. The initial temperature was taken by him to be of the form

$$T_0 = S_0 + mx$$

where S_0 is the initial surface temperature and m is the initial gradient at the time of solidification; bearing in mind the effect of pressure on the melting point of rocks, HOLMES adopted $m = 5 \times 10^{-5}$ deg/cm, $S_0 = 1000°$. In HOLMES' solution ε_0 is taken as $6{\cdot}39 \times 10^{-13}$ cal/cm^3 sec corresponding to the values available at that time for the rate of heat generation in granites (present values are somewhat lower); $h^2 = 7 \times 10^{-3}$ cm^2/sec. The present surface heat flow is used to determine the parameter a which turns out to be 4×10^{-7} cm, i.e. the radiogenic heat at 16 km depth is $\frac{1}{2}$ that at the surface. HOLMES used INGERSOLL and ZOBEL's (1913) solution of equation (1) to find T down to 100 km, at which depth the temperature turned out to be 1575°C. On HOLMES' model, about $\frac{3}{4}$ of the heat escaping at the surface is radiogenic, $\frac{1}{4}$ being contributed by the original heat content at the time of solidification and subsequent cooling. It is interesting to note HOLMES' use of an exponential function for ε; this is still the best form we have. HOLMES was lead to adopt this form by RAYLEIGH's (1906) remark that radioactive matter must be notably concentrated towards the surface of the earth. If it were uniformly distributed in an upper layer of acidic (sialic) rocks, this layer could not exceed 19 km in thickness without producing more heat than actually escapes, and HOLMES noticed that the temperature at its base would only be 300°C; this, to HOLMES, was inconsistent with the temperature required to explain volcanism. Similarly, a crust with radioactive content equal to the average for granite and basalt could not be more than 30 km thick, and the temperature at its base would be 530°. Thus radioactivity must decrease in depth and the decrease must be very rapid to allow the radioactive elements to persist to sufficient depths to give the requisite temperatures for surface lavas (ca. 1200°C). The argument, as we now see it, is fallacious; eruption of lava at 1200° does not mean that there exists a world-encircling layer from which these lavas are derived and which is everywhere and always at this temperature. Volcanism is localized in place and time.

Adams' Contribution

ADAMS (1924) re-examined more closely the question of initial temperature distribution in an earth cooling from the liquid state. He pointed out that so long as

the mantle remained liquid, convective equilibrium would obtain and the temperature gradient would be close to the adiabatic one, $\frac{dT}{dx} = \frac{\alpha T g}{c_P}$. [This relation is easily obtained from the thermodynamic expression for (dT/dP) at constant entropy and the hydrostatic relation $dP = g\rho dx$.] The adiabatic gradient, according to ADAMS, would be close to 1·1°/km. Now convection would proceed until the mantle had cooled to an extent such that either its viscosity would have become so large that further motion would be impossible, or such that it would solidify. Assuming a logarithmic dependence of viscosity on pressure, ADAMS found that the gradient required to maintain a constant viscosity would probably be 1 to 10°/km, whereas the melting point gradient would be between 2·5 and 5°/km. The adiabatic gradient being less than either of these figures, ADAMS concluded that convection would be terminated at the bottom, i.e. the mantle would crystallize from the bottom up; he did not, however, exclude entirely the possibility that below 2000 km viscosity would be the controlling factor in terminating convection. The important point is that the initial temperature in the upper 2000 km when convection ceased and conduction became important would be the melting point. From here on, ADAMS' calculations follow along the lines of HOLMES', but with slightly different constants. He took $t_0 = 1{\cdot}6$ billion years, $S = 1400°$, $m = 4°$/km and found $a = 5 \times 10^{-7}$. His temperature distribution in the upper region runs slightly below that of HOLMES (1300° at 100 km against 1575° in HOLMES' calculations); he extended the curve to 300 km depth where he found a temperature of 2400°C.

Jeffreys' Solution

In 1916 JEFFREYS (1916) had proposed a solution based on a single radioactive surface layer and no radioactivity below it. In 1929 he revised this solution to include the subdivision of the crust into the two layers that seismology had recently revealed; he later (1952) returned to the exponential distribution, as he could see no reason to believe that the mantle is quite free from radioactivity. His parameters are, again, slightly different from those of ADAMS and HOLMES. Although he used the same value of $t_0 = 1{\cdot}6\ 10^9$ years, he adopted $m = 3°$/km. The calculations, based on a one dimensional analysis as for the cooling of a flat plate, are extended to a depth of 700 km, and the temperatures he finds are slightly lower than those of HOLMES or ADAMS (see Table I). Note that JEFFREYS' 1929 figure, which is reproduced without change in the 3rd edition of *The Earth*, takes no account of cooling due to the m term in the initial temperature distribution; this would be: $3mh^2t/R$ for depths over 380 km and would amount to 50° or so. Cooling becomes inappreciable at a depth of about 700 km.

Two aspects of JEFFREYS' contribution need emphasis: in the first place he called attention to the uncertainties involved in the various parameters m, k, S_0, etc. Secondly he called attention to regional variations in radioactive content of surface rocks and hence to the difficulty in choosing adequate values of ε for the upper layer and particularly for the lower layer, the existence and petrological nature of which are still in doubt. This is mainly the reason why he returned in 1952 to the exponential distribution, still insisting on the uncertainty arising from inadequate sampling.

BULLARD (1939) has cast JEFFREYS' solution for a layered crust in the slightly different form

$$T = T_0 + AQ\bar{x} \qquad \ldots.(2)$$

where $T_0 = mx + S_0 \operatorname{erf}(x/2h_1t^{\frac{1}{2}})$ is the temperature that would obtain in the absence of radioactivity, $A = [1 - \operatorname{erf}(x/2h_1t^{\frac{1}{2}})]/k$, $Q = \int_0^\infty \varepsilon dx$ and $\bar{x}$ is the depth of the centroid of the distribution of radioactive matter, or mean depth of radioactive matter; k is the thermal conductivity of the radioactive layer and h_1^2 is the diffusivity below the radioactive layer. Q is known if the surface heat flow has been measured; the temperature at any depth will then only depend on $\bar{x}$. Following results for the temperature at a depth of 50 km are obtained for $Q = 1 \times 10^{-6}$ cal/cm² sec, corresponding to a heat flow of $1{\cdot}25 \times 10^{-6}$ cal/cm² sec.

$\bar{x}$	T_0	$AQ\bar{x}$	T
5	380	100	480
10	380	210	590
20	380	420	800
30	380	630	1010

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These results clearly show the effect on temperature at a given depth of an increase in the mean depth of the radioactive matter. If the temperature is to be everywhere less than at the time of solidification, $T < S_0 + mx$ and

$$\frac{Q\bar{x}}{k} < S_0$$

which, with values adopted by BULLARD, gives $\bar{x} < 70$ km. If $\bar{x}$ were greater than this, heating and therefore remelting would occur.

Slichter's Contribution

It must now be clear to the reader that the temperature distribution that will emerge from calculations of this kind will largely depend on the choice of parameters. The problem was therefore considered in more general terms by SLICHTER (1941) who computed final steady-state temperature distributions for a number of different earth models. The range of values he finds is indicative of the importance of making correct assumptions. SLICHTER computes, for instance, that the steady state temperature at the centre of the earth could be anywhere between 279° and 63,700° depending on the choice of k and ε at various depths [note that such final steady state temperatures would never be reached, as SLICHTER ignores the variation of ε with time; as the total amount of radioactive material in the earth steadily decreases with time, the only possible steady state is $T = 0$ everywhere]. SLICHTER further emphasized the extraordinarily large thermal inertia of the earth resulting from its large size and small diffusivity. If heat is transferred by conduction, any sudden change in temperature at the surface would leave the temperature at the centre unaffected for 200 billion years, and vice-versa. The present surface heat flow is essentially due to thermal events in the few upper hundred kilometres; no heat generated below that level has yet reached the surface. It follows that even granting excellent thermal information about the crust it is possible to deduce by thermal theory only very limited information about regions below a depth of 200 or 300 km. Contrary to commonly accepted views, significant concentrations of radioactive material may exist all the way to the centre without violating known criteria. It follows also that the rate of cooling below 500 km is only about 30 to 120° per

billion years; such a small rate of heat loss could be compensated by a radioactive heat generation of about 1 to 4 $\times$ 10^{-15} cal/cm^3 sec. The rate of heat generation in stony meteorites from potassium alone is about 3 $\times$ 10^{-15} cal/cm^3 sec at present (BIRCH 1954) and was considerably larger 2 billion years ago. Comparison of the two figures shows that it is possible, and even probable, for heating to occur at a rate greater than the rate of cooling. It would thus appear likely that the earth may be cooling at shallow depths, but heating at greater depths.

Urry's Time-dependent Solution

Recent years have seen the development of new ideas regarding the origin of the earth and its possible formation as a cold body (URRY, 1952; LATIMER, 1950; BROWN, 1952). At the same time its age has been extended from 1·6 10^9 to 3·3 and finally to about 4·5 10^9 years (PATTERSON, 1953; WASSERBURG and HAYDEN, 1954). For such a long-lived earth, the increase in radiogenic heat in early times becomes very important. URRY and COMENETZ accordingly computed solutions of equation (1) including the dependence of ε on time. Full results have not been published, to the reviewer's best knowledge, but a condensed summary of results appeared in URRY (1949). It appears from URRY's results that the thermal history of the earth may have been far more complex than was previously recognized. General cooling may have been preceded by a period of heating, and there may have been simultaneous heating at one depth and cooling at another. Even if the earth formed in a cold state by collection of solid particles at a rate sufficiently slow to allow gravitational heat to be radiated away, it remains possible for the earth to have heated up to the melting point in a time estimated by URRY to be of the order of 3 or 4 billion years. BIRCH (1951), using more recent data on the decay constant of K^{40}, has estimated that the time required for remelting could be as short as 1 billion years; this result must now be slightly revised upward to correspond to the presently accepted value (0·1 per cent) of the K-content of stony meteorites. [Their uranium content is small (PATTERSON, 1953; DAVIS, 1950).]

Gutenberg's Depth-temperature Curve

GUTENBERG (1939) suggested that the temperature in the mantle is considerably lower than the previous estimates of HOLMES, ADAMS, or JEFFREYS. The Gutenberg curve is not based on exact calculations; it is, in GUTENBERG's own words, very tentative. GUTENBERG estimated that convection currents would have reduced the gradient in the mantle at the time of crystallization to the adiabatic value; why the gradient at the time of solidification could be less than the melting point gradient is not explained. GUTENBERG points out, in addition, that the thermal conductivity in the mantle is probably noticeably larger than in surface rocks; this would further contribute to a reduction of the gradient.

Jacobs' Solutions

JACOBS (1954) recently announced that he has computed solutions of the heat conduction equation, including the dependence on time of radioactivity, for an earth consisting of a number of shells of different, though uniform, radioactive content. The calculations have been so arranged that the actual amount of radioactive material in each shell does not appear in the details of the computation. Tables have been drawn up so that a solution may easily be written down

for any desired concentration of radioactive material in any of the shells. Temperatures and heat flows have been evaluated at a number of depths and at a number of different times. Calculations were carried out on the assumption of a constant thermal diffusivity.

THERMAL CONDUCTIVITY

Whether the earth initially formed from the liquid state, or formed from solid particles which later remelted, the heat loss by conduction at depths greater than 500 km or so would be very small and the temperature at such depths would still be very close to the melting point, so close in fact that even the small amounts of radioactive elements present in meteoritic matter would suffice to completely offset the cooling (see above, p. 22) and cause remelting. In fact, as pointed out by BIRCH (1954), the condition that the mantle now be solid puts a more stringent limit on the amount of radioactivity in the deep mantle than the present surface heat flow. BIRCH's figure needs to be slightly modified because he takes 500 cal/g as the total heat of melting from low temperature. This figure, although correct at zero pressure, must be multiplied by 2 or 3 in the deep mantle where the melting temperature is probably around 5000° (see p. 27). It remains, however, difficult to see how the deep mantle, if it ever was near its melting point, could have cooled sufficiently to prevent remelting. One way out of this dilemma would be to greatly increase the thermal diffusivity, allowing thereby a great rate of cooling. It is important, therefore, to examine more closely the possible variation of diffusivity with depth, and particularly the effect of pressure on it.

The diffusivity h^2 is defined as $k/\rho c_P$. ρ is known with sufficient accuracy at all depths from the theory of the figure of the earth and seismology. c_P is less exactly known, but its variations with temperature and pressure have been carefully examined by BIRCH (1952), who concludes that they are small. The main uncertainty arises from k.

Unfortunately the prediction of the thermal conductivity of a dielectric substance and its variations with P and T constitutes one of the most difficult problems in solid state physics. It is well-known that thermal conductivity is in itself a second-order effect which arises from the anharmonic terms, that is, from cube and higher power terms in the expression for the potential energy of the solid as a function of particle displacements; these same anharmonic terms determine the thermal expansion, departures from Hooke's law, and departures of the high temperature, constant-volume specific heat from its classical value $3k$ per particle. These terms, however, if taken alone, lead to an infinite conductivity (HERPIN, 1954); one must consider also the effects of lattice defects and of the finite size of crystals. It has indeed been shown experimentally that the thermal conductivity of very small crystals depends on their size; for larger grains it is presumably determined by the size of the mosaic blocks, i.e of the regions over which the crystal maintains a perfect lattice and constant orientation. This dependence on structure explains in part measured differences in thermal conductivity of different specimens of the same substance. UFFEN (1952; 1954) has applied the simplified Debye theory to the variation of k in the mantle. This leads to the interesting result that k may be eight times as large, and h^2 may be four times as large at the bottom of the mantle as for the

same material at 100 km depth. These figures are uncertain by a factor of 2 or 3 or more. If, as appears possible, the thermal conductivity at great depths is ten or twenty times larger than the accepted values, all numerical calculations regarding the thermal history of the earth may need to be revised to provide for greater cooling at depth and for an increase in the contribution from residual heat to the present surface heat flow.

DISTRIBUTION OF RADIOACTIVE MATTER; HEAT FLOW UNDER THE OCEANS

BULLARD's equation (2) shows that the temperature distribution is largely determined by the total amount of radioactive material Q, which may be determined from the surface heat flow, and by the space distribution of this material represented by $\bar{x}$. It would be important to estimate $\bar{x}$ independently.

The heat flow in continental areas is the sum of three terms representing, respectively, the heat Q_c generated in the continental (sialic) masses, the heat Q_m generated by radioactivity in the mantle down to a certain depth depending on the thermal conductivity (cf. SLICHTER's remark that deep seated radioactivity does not contribute to the present heat flow), and residual heat Q_i down to the same depth. It is usually believed, from analyses of continental rocks and their radioactive content that Q_c is by far the larger of the three terms. One would thus expect that the heat flow in oceanic areas where there is no sialic layer would be appreciably smaller than in continental areas, and the difference would give some indication as to the actual distribution of radioactive material in the crust

This expectation is not borne out by measurements. BULLARD (1954a, b) reports from five stations in the North Atlantic values ranging from 0·58 to 1·42 μcal/cm^2 sec (1 μcal = 10^{-6} cal), with an average of about 1 μcal/cm^2 sec [the average for continental areas is close to 1·25 μcal/cm^2 sec]. REVELLE and MAXWELL (1952; MAXWELL and REVELLE, 1955) found in 1950 an average of 1·12 for six stations in the North Pacific. Nine measurements in 1952–53 gave an average of 1·4, with large variability (from less than 1 to nearly 3). Further measurements (REVELLE, 1955) in 1954 gave low values (0·75) in the neighbourhood of the Acapulco trench. They also confirm previous high values (about 3 μcal) in the Albatross Plateau; three new values in the basin west of the Plateau are around 1·2. All the 1950 measurements but one were made near the Mid-Pacific Mountains where there is no evidence of recent volcanism. The contribution from the sediments and rocks above the Mohorovičić discontinuity, which is at a depth of about 10 km below sea level, is small, so that $Q_i + Q_m$ must, on the average, be close to 1 μcal/cm^2 sec or more. MAXWELL and REVELLE (1955) note that, disregarding residual heat, the heat flow would correspond to an average rate of heat production in the oceanic mantle of $0{\cdot}58 \times 10^{-14}$ cal/cm^3 sec; this is about equal to the heat generation by K^{40} in stony meteorites (BIRCH, 1954), taking into account the higher density of the mantle. Heat generation in an olivine (dunite) mantle would be less.

There are, however, strong geochemical and petrological considerations against the concept that the mantle consists entirely of olivine. In the first place, no common type of lava or igneous rock could ever derive from a dunitic mantle. Secondly, the mean composition of the earth would notably depart from

meteoritic or cosmic composition, particularly with regard to aluminum and the alkali metals. A dunitic, or peridotitic, layer could be formed by fractional crystallization or fractional melting of meteoritic material; the difficulty is that, as an average stony meteorite is equivalent in chemical composition to about 75 per cent peridotite and 25 per cent basalt and granite, a large fraction of the mantle should thus consist of basalt which does not appear to be present at all.

The similarity in heat flow in continental and oceanic areas suggests that the average composition beneath these areas might be very similar. This would be consistent with the idea that continents have gradually grown by partial remelting of an initially uniform meteoritic mantle [see HURLEY (1951), RUBEY (1951)], the easily fusible sialic constituents of which would rise to the surface and carry with them the largest part of the radioactive elements of the meteoritic material. We note, however, that it is not sufficient that the average composition down to the core be the same in continental and oceanic areas. It must be the same in the upper few hundred kilometres which are now contributing to surface heat flow (see discussion of SLICHTER's contribution). If heat transfer is mainly by conduction, radioactive material in the lower mantle contributes but very little to the present heat flow. It can also be shown that radiogenic heat in a uniform mantle of meteoritic composition would lead in a short time to melting at depth, if it ever was near its melting point. MAXWELL and REVELLE thus go on to show that if the oceanic heat flow is due to conduction of radiogenic heat, the radioactive content of the upper 160 km or so must be about $\frac{1}{3}$ that of basalt, or many times that of stony meteorites. This, however, would lead to temperatures between 100 and 300 km substantially (about 500°) higher than at corresponding depths in the mantle below continents. Such large temperature differences would lead to differences in density of about 1 per cent, which would be difficult to reconcile with presently held views on isostatic equilibrium, the gravity field and the theory of the figure of the earth. It is, in addition, very difficult to see how any upward concentration of radioactive elements could occur in the oceanic mantle without accompanying petrological differentiation that would be reflected in notable differences in travel times of seismic waves below oceans and continents.

A more likely situation, according to MAXWELL and REVELLE, is that the thermal conductivity in the deep mantle may be high (see p. 23). This, however, requires a low initial temperature; for if the initial temperature were high with k high, the residual heat flow plus the radiogenic heat would be larger than the observed heat flow.

MAXWELL and REVELLE suggest that convection could provide a suitable alternative. It has been shown by SLICHTER (1941) that heat transfer by convection is likely to be much more rapid than by conduction for large size of the circulating units, even if the rate of motion is only of the order of a few centimetres per year. [Note, however, BROOKS' discussion (1941) of intermittent convection and its efficiency as heat carrier.] Convection is thus equivalent in its effects on temperature to a greatly enhanced conductivity. It is also equivalent to a variable conductivity, in the sense that convective transport increases with increasing thermal gradients. Continuous convection would, however, lead to larger heat flows than observed if the initial temperature were high; it would also lead to a pattern of high and low rates of heat flow corresponding respectively to ascending and descending currents. Intermittent convection, the last phase of which

might have occurred 100 million years ago or so, might result in the proper temperature distribution and heat flow at the present time. Similarity of continental and oceanic heat flow values would, in this case, be purely accidental. BULLARD (1954a) reaches similar conclusions regarding the part convection may play in heat transfer under the ocean.

It remains difficult on any assumption to reconcile the heat flows in continents and oceans. It may be that the radioactivity of continental masses has been largely overestimated. Granites may on the average be less radioactive than surface sampling suggests. Geological evidence serves to indicate that continents may consist dominantly of metamorphic rocks rather than of granites; very little is known on the distribution of radioactive matter in metamorphic rocks. It is also possible that the average oceanic heat flow is less than available determinations would suggest. Finally, it may also be that a reconsideration of seismic and gravity data will allow for larger average temperature differences in oceanic and continental sectors of the mantle. Whatever the outcome may be, oceanic heat flows strongly suggest that either conduction is not the dominant process of heat transfer, or that assumed distributions of radioactive matter in continental areas need be revised. In either case, temperature calculations based on the heat conduction equation need to be considered with extreme caution.

MELTING AND TRANSFORMATION POINTS

If it could be established that a certain seismic discontinuity within the earth corresponds to a given phase transition (e.g. melting), knowledge of the temperature at which this transition occurs would, obviously, determine the temperature prevailing at the discontinuity. The effect of pressure on the transition temperature must, of course, be considered.

Down to 2900 km the mantle behaves like a solid of high elasticity; it is a safe inference that its temperature at any depth is less than the melting point at that depth of its most easily fusible constituents. As we have seen, the melting point gradient also plays a prominent part in earlier theories of the earth's thermal history. Great interest attaches to the correct value of this gradient.

The change with pressure of the melting point of a pure phase is given thermodynamically by the well-known Clapeyron equation

$$\frac{dT_m}{dP} = \frac{\Delta V}{\Delta S} \qquad \ldots.(3)$$

where ΔV and ΔS are, respectively, the volume and entropy changes upon melting. Experimental determinations are available for a number of important minerals. The initial slope of the melting point is 4·7°/1000 bars for forsterite Mg_2SiO_4 (BOWEN and SCHAIRER, 1935), 13°/1000 bars for diopside $CaMgSi_2O_6$ (YODER, 1952) and 26°/1000 bars for albite $NaAlSi_3O_8$ (GORANSON, 1938); similar figures for other minerals may be computed from data in the *Handbook of Physical Constants* (BIRCH, *et al.* 1942). The initial slope is likely to be appreciably reduced by increasing pressure, for the compressibility of the liquid is usually higher than that of the corresponding solid and ΔV decreases; ΔS, on the other hand, contains a purely configurational term that is not likely to be much affected by pressure (VERHOOGEN, 1954). A mantle consisting entirely of olivine would probably have an average melting point gradient not greater

than 3·5°/1000 bars, which would be much less than the gradient of 3°/km adopted by JEFFREYS (see p. 20); it is, however, much more difficult to predict the behaviour of a multi-component system.

Melting Point in the Mantle

UFFEN (1952) has recently computed the melting point in the mantle, using LINDEMANN's theory which relates the melting temperature to a characteristic frequency of lattice oscillations. UFFEN uses DEBYE's theory of solids to compute this frequency from elastic constants obtained from the velocities of elastic waves through the mantle. He finds

$$\frac{T_{mh}}{T_{mo}} = \frac{\phi_h}{\phi_o}$$

where T_{mh} is the melting point at depth h, T_{mo} is the melting point at some reference depth (100 km) and $\phi = K_S/\rho$ is the ratio of incompressibility to density; it is obtained directly from the relation $\phi = v_p^2 - \frac{4}{3}v_s^2$. By this method the melting point at 2900 km depth turns out to be 2·92 times that at 100 km depth; this would set the melting point at the bottom of the mantle at about 5000°K. UFFEN's method has the great advantage that it does not require a precise knowledge of the chemical or mineralogical constitution of the mantle. It has, however, the disadvantage that the melting point so determined is that of the most abundant constituent, i.e. that which most affects the elastic velocities; this is not necessarily the most fusible one. Partial melting could possibly occur at a lower temperature than determined by this method.

Melting Point of Iron

SIMON (1953) has recently computed the melting point of iron at very high pressures. His calculation is based on experimental data for the change in melting point under pressure of substances (e.g. helium) with very low melting point which can be investigated over a wide range of pressure. These substances are found to obey the law

$$P/\alpha = (T/T_0)^c - 1 \qquad \ldots.(4)$$

where c is a constant and α is simply related to the internal pressure $-\left(\frac{\partial U}{\partial V}\right)_T$, U being the internal energy. By combining (4) and (3), one gets a relation between c and α, provided that the initial slope of the melting point curve be known. For alkali metals the ratio $\alpha \Big/ \left(\frac{\partial U}{\partial V}\right)_T = 1{\cdot}5$. We also have $\left(\frac{\partial U}{\partial V}\right)_T = \gamma \frac{c_v T}{V}$ where c_v is the constant volume specific heat (per mole), V is molar volume and γ is GRUNEISEN's ratio; all these quantities being known for iron, α may be estimated assuming its ratio to $\left(\frac{\partial U}{\partial V}\right)_T$ to be the same as for the alkali metals. SIMON determined the temperature at the inner core boundary (5100 km depth) as 3900° ± 200°K, assuming the discontinuity at that depth to correspond to a liquid-solid transition. The melting point of iron at the pressure obtained at the base of the mantle is about 3000°K. JACOBS (1954) has shown that the

existence of an inner core made of solid iron could easily be understood on the basis of SIMON's results. If the boundary between the outer core and the inner core at a depth of 5100 km effectively corresponds to a liquid-solid transition, the temperature at that depth would be 3900°K. The density jump at the boundary, as determined from SIMON's melting point gradient, would be quite small, notably less than required in BULLEN's (1950) model B. Again, if the inner core is solid iron, the temperature at the centre of the earth cannot be greater than 4100°K, which is the melting point of iron at the corresponding pressure. The reason for the occurrence of a solid inner core is, according to JACOBS, that the melting point gradient for iron is larger than the adiabatic gradient in the outer, liquid, core. There is considerable uncertainty concerning this adiabatic gradient. BULLARD (1948; 1950) initially determined it as 1·1°/km. He used, however, a temperature of 10,000°C, which now appears too high; since the adiabatic gradient is proportional to T, reducing the temperature from 10,000 to 4000° would appreciably reduce the gradient. VALLE (1951; 1952) determined the adiabatic gradient in the core from an extrapolation of DEBYE's theory (see below), and found a ratio $T_{5000}/T_{2900} = 1{\cdot}38$, where subscripts refer to depth in kilometres. For $T_{2900} = 3000°$K (the lower limit), this gives an average gradient in the outer core of 0·5°/km; but for $T_{2900} = 5000°$K (the upper limit), the gradient is 0·9°/km. JACOBS (1953) used the empirical relation $1/\alpha = C + bP$ (where α is thermal expansion, C and b are constants) which he finds to apply in the mantle and which is similar to the relation involving the incompressibility K

$$K = K_0 + aP$$

which BULLEN (1954) derived from seismic data. BULLEN finds that this relation also applies to the outer core, and JACOBS accordingly extrapolates his similar relation for α. He further assumes c_P to be constant and finds a ratio $T_c/T_{2900} = 1{\cdot}11$ where T_c is the temperature at the centre of the earth for adiabatic conditions. This ratio is considerably less than the ratio $T_{5000}/T_{2900} = 1{\cdot}38$ obtained by VALLE, and the validity of JACOBS' extrapolation is questionable. The temperature at the inner core boundary being 3900°K, as determined by SIMON, JACOBS concludes that the temperature at the outer core boundary must be 3600°K; VALLE's ratio would give 2900°K under the same assumptions. As noted above, the temperature at the centre of the earth on this hypothesis cannot be greater than 4100°K, which is the melting point of iron at the corresponding pressure. From this JACOBS further deduces that the melting point in the mantle at the core boundary cannot be greater than 3680°K; the base of the mantle would thus still be almost at its melting point. The same sort of reasoning, using VALLE's ratio, would give a melting point of less than 3000°K, which would seem rather low. UFFEN and MISENER (1954) similarly deduce from SIMON's results that the temperature at the core boundary lies between 3000 and 5000°K.

These calculations are based (*a*) on fairly uncertain values of the adiabatic gradient in the core, (b) on the assumption that both the inner and outer cores, consist of pure iron, and (c) on SIMON's determination of the melting point of iron. Different views have been expressed regarding assumption (b) (RAMSEY, 1949; BULLEN, 1952), which nevertheless remains a plausible one (BIRCH, 1952). Regarding assumption (c), it should be noted that SIMON, like LINDEMANN, considers the melting point to be entirely determined by properties of the solid

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phase. It could be argued that melting represents an equilibrium between solid and liquid; hence the properties of the liquid and their change with pressure should be just as important as those of the solid; it is well known that similar solids may have remarkably different melting points because of differences in the corresponding liquids. There is no doubt, however, that SIMON's determination of the melting point of iron now represents the best available datum.

Diamond

A suggestion regarding the temperature prevailing in the upper mantle arises from the occurrence of diamond in rocks such as kimberlites and eclogites that have been brought to the surface from depths which are great on the geological scale but are not likely to be much greater than 100 or 200 km. The equilibrium between diamond and graphite is such (GORANSON, 1940) that if diamond exists stably at depths less than 300 km ($P < 100{,}000$ bars), the temperature must be less than 1700°C; if diamond comes from depths less than 150 km, the temperature at that depth cannot be greater than 1100°C. These maximum temperatures are somewhat lower than those given by JEFFREYS.

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Melting in the Mantle

UREY (1952) has recently proposed a temperature distribution based on an earth model with the following characteristics. In the region below the crust to about 200 km depth some melting of silicates occurs. Below this region to about the 900 km depth both silicate and iron phases are present and are crystalline. Below the 900 km depth the iron phase, forming less than about 13 per cent by volume, is liquid. At the 5000 km depth the iron, or ion-nickel alloy, again solidifies and produces the inner core. The temperature curve required to fit this model rises rapidly in the upper mantle to reach about 2200° at 250 km depth and 2700° at 500 km; below this point the gradient is approximately adiabatic, with a temperature of 3000° at about 1100 km (UREY's curve was drawn before SIMON published his results, according to which the melting point of iron at 900 km depth could only be 2100°C). Note that in UREY's model the temperature between approximately 40 and 375 km is above the melting point of basalt. As basalt forms about 25 per cent of average stony meteorite material, it is difficult to see what would prevent this abundant liquid from rising by virtue of its low density and forming a world-encircling layer of molten or glassy lava. The idea that such a glassy basaltic layer might exist was very popular among geologists at one time, although many objections were raised [BOWEN (1928) pp. 311–15]. The idea has generally been discarded since the appearance of BIRCH and BANCROFT's (1942) work on the elasticity of glass at high temperature. The elasticity of the mantle is so high that it is extremely unlikely that more than a very small fraction could be molten. UREY's temperature curve is based on an *ad hoc* model of the earth for which there is no collateral evidence. The same remarks apply to DALY's (1943) 1943 temperature distribution which is based on the assumption that there is a transition from crystalline to vitreous peridotite at a depth of 70 km, and a further change to crystalline material at 450 km. VON WOLFF (1943) similarly assumes a transition at 70 km to an amorphous state and a further transition at 2900 km to a "chaotic, i.e. gaseous" state. According to VON WOLFF the temperature in the mantle below 70 km is everywhere greater than the melting point of olivine. The uncertainty regarding the

nature of phase transitions, if any, in the upper mantle and their pressure dependence is such that calculations of this type are most unreliable. VON WOLFF's views were criticized by EUCKEN (1944) who concluded that all that can be said regarding the temperature at the centre of the earth is that it lies between 3000° and 10,000°.

The temperature distributions suggested by HOLMES, ADAMS, and JEFFREYS also seem to lead to difficulties regarding melting. Their temperatures are, to be sure, everywhere less than the original temperature, which was assumed to correspond to the melting point. It has already been pointed out that these solutions, which are based on an exponential decrease in radioactivity with depth, ignore the small but possibly significant radiogenic heat that may be present at great depths where cooling has been negligible; this heat would necessarily lead to remelting after a certain time. There are also difficulties connected with the very steep gradients in the upper mantle. No remelting would occur in this zone if the mantle consisted entirely of olivine (dunite) or of olivine + pyroxene (peridotite). On the other hand, it is difficult to see how basalt could ever be produced from a mantle of this type which would be almost completely devoid of alkalies and poor in alumina. The only convenient way to produce basaltic magma seems to be partial fusion of stony meteorite material (BOWEN, 1928), the melting point of which extends over a wide temperature range beginning at the melting point of basalt itself. Even allowing for a substantial reduction under pressure of the melting point of basalt as given by YODER (1952), the HOLMES, ADAMS, and JEFFREYS' curves would lead to a permanently molten state of the basaltic fraction of the upper mantle. It may be, of course, that there is no such fraction. Petrological evidence on the nature of inclusions brought up by basaltic lava flows all over the world, and the extraordinary similarity of these olivine nodules to the common peridotites of orogenic zones (ROSS, *et al.* 1954) strongly suggest that the upper mantle consists indeed of peridotite which, in turn, can be interpreted to be the residue of the original meteoritic material from which the low-melting fraction has already been separated by partial fusion and now forms the crust. RUBEY's (1951) calculations based on the present volume of the crust suggest that this process of fractional melting has so far only affected a small part of the mantle. The temperature now has to be less than the melting point of the lower melting fraction in the undifferentiated portions of the mantle, but could be higher in the differentiated parts. If differentiation is complete down to depths of several hundred kilometres, no difficulty arises; but if undifferentiated portions still occur within, say, 100 or 200 km of the surface, the temperature at those depths would have to be somewhat less than calculated to avoid melting.

TEMPERATURES BASED ON SEISMIC DATA

The pressure at any depth x inside the earth is, for hydrostatic equilibrium

$$P = \int_0^x g\rho dx.$$

It would appear at first sight that the pressure distribution will be sensitive to the density distribution, which is not exactly known. This, fortunately, turns out not to be the case, for g also depends on the density distribution in such a

way that P is nearly independent of it. Any density distribution that leads to the correct mass and moment of inertia for the earth as a whole leads to about the same value of the pressure. To this extent, the pressure may be considered to be an independent datum.

If, then, we knew the initial density and the equation of state $\rho = f(T, P)$ for the earth-forming materials, this equation could be solved for T, given P and ρ at any depth. Unfortunately ρ is not uniquely determined by the seismic data, and the uncertainty which is of the order of a few per cent is precisely of the same order as the temperature effect which we try to determine. This effect would be indeed of the order of $0{\cdot}03\rho$ to $0{\cdot}2\rho$, since $\alpha \approx 10^{-5}$ and $T \approx 10^3 - 10^4$.

The quantity $\phi = K_s/\rho$ may be found at any depth, without any additional hypotheses, from seismic data, since $\phi = v_p^2 - \frac{4}{3}v_s^2$ where v_p and v_s are, respectively, the velocities of longitudinal and transverse elastic waves. If the quantity ϕ could be computed from the equation of state as a function of P and T, knowledge of ϕ at any depth where P is known would give T. The difficulty is, however, that most equations of state give ρ as a function of P at constant temperature. Thus, one may compute K_T/ρ where K_T is the isothermal incompressibility, but not K_S/ρ which involves the adiabatic incompressibility. The relation between the two is

$$K_S = K_T(1 + T\alpha\gamma)$$

where $\gamma = \dfrac{\alpha K_T}{c_V} = \dfrac{\alpha K_S}{c_P} = \dfrac{\alpha}{c_P}\phi$ is GRÜNEISEN's ratio. As, in addition, the composition of the mantle is not known, knowledge of ϕ and P as a function of depth is insufficient to determine T.

Miki's Temperature

In spite of such inherent difficulties, MIKI (1954) has computed values of T in the mantle for certain assumed values of its mean atomic weight and for $\gamma = 1{\cdot}5$ and $\gamma = 2$. He did not consider the case $\gamma = 1$ which is the most likely (BIRCH, 1952; UFFEN, 1952). It appears also that the temperature MIKI obtains is the difference between two large numbers, both of which are of the order of 10^5, and quite uncertain. MIKI further adopts the hypothesis that c_V has its high-temperature classical value of exactly $3k$ per particle. This is probably incorrect because in the first place the temperature in the mantle is not sufficiently larger than the Debye temperature, and secondly because of anharmonic terms which are already present in the specific heat curves of forsterite and fayalite at ordinary pressure (VERHOOGEN, 1955). Clearly, MIKI's values are to be regarded only with extreme suspicion.

Birch's Analysis

BIRCH's analysis (1952), by far the most detailed and comprehensive to date, leads for a homogeneous body to the relation

$$1 - \frac{1}{g}\frac{d\phi}{dr} = \left(\frac{\partial K_T}{\partial P}\right)_T + AT\alpha\gamma + B(T\alpha\gamma)^2 + C\frac{\alpha\phi\tau}{g}$$

which embodies all available information. In this relation τ is the actual temperature gradient minus the adiabatic gradient; A, B and C are combinations of the dimensionless parameters $\dfrac{1}{\alpha K_T}\left(\dfrac{\partial K_T}{\partial T}\right)_P$, γ, $\left(\dfrac{\partial K_T}{\partial P}\right)_T$, $\dfrac{1}{\alpha^2}\left(\dfrac{\partial \alpha}{\partial T}\right)_P$,

$\frac{1}{\alpha c_P}\left(\frac{\partial c_P}{\partial T}\right)_P$. If these parameters were known, the left-hand side could be evaluated from seismic data, and the equation solved for T, given the value of T or τ at any one depth. The parameters, however, are small dimensionless quantities of the order of a few units, and are difficult to evaluate; there may be some uncertainty as to the signs of A, B and C, let alone their magnitude. BIRCH (1952) has attempted to evaluate $\left(\frac{\partial K_T}{\partial P}\right)_T$ from an equation of state based on finite strain theory. Whether this particular equation of state is applicable or not to silicate materials is open to doubt (VERHOOGEN, 1953), but there is no doubt that to the first order $1 - \frac{1}{g}\frac{d\phi}{dr} = \left(\frac{\partial K_T}{\partial P}\right)_T$. All terms involving T and τ are of the second order, and their evaluation would require far more refined theories of the solid state than we now have. BIRCH concludes that all that can be inferred from seismic data is that a temperature of the order of 5000° in the deep mantle would not be inconsistent with these data; a temperature of 10,000°, as suggested by BULLARD (1948) and ELSASSER (1950) seems definitely too high.

So far no use has been made of the fact that seismology really provides us with two independent data: v_p and v_s. These velocities are functions of the elastic coefficients K_S and μ (rigidity), and of the density ρ. Let us assume again that these three quantities are only functions of P, T and a parameter c describing the crystal structure and composition; since P is independently known, we would have two equations to solve for T and c. The difficulty again is that the dependence of μ on P and T is even less well known than that of K. BIRCH (1939) indicated how the variation of μ with P could be obtained from finite strain theory, but noticed (1952) that μ is sensitive to third order terms in the strain energy function which are difficult to evaluate. The problem is further complicated by uncertainties regarding the homogeneity of the upper mantle and the variation of ϕ as a function of r in its upper few hundred kilometres.

Thermal Expansion

VERHOOGEN (1955) has noticed that the thermal expansion at normal pressure of a large number of substances obeys the empirical relation

$$\alpha T = b\left(\frac{T}{\theta}\right)^{3/2}$$

where b is a dimensionless constant and θ is the Debye temperature at temperature T as obtained from specific-heat measurements. b is independent of T but varies with P, the relation being

$$\frac{K_T}{b}\frac{db}{dP} = \frac{1}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right)_P + \frac{3}{2}\gamma$$

and uncertainties on the values of γ and $\frac{1}{\alpha K_T}\left(\frac{\partial K_T}{\partial T}\right)_P$ in the mantle again forbid a rigorous solution. It is possible, however, to set a reasonable upper limit to these two parameters and obtain a minimum value of b. Since θ can be computed from seismic data, using DEBYE's expression for the dependence of θ on elastic velocities, it is possible to get a maximum value for T at the core boundary which turns out to be about 2700°K. This estimate is uncertain because, in the

first place, α is not accurately known; only $\frac{\alpha}{c_P}$ can be obtained from seismic data (see below). Furthermore, it is well known that the values of θ derived from elastic constants and specific heat rarely agree. As the temperature is proportional to θ^3, a small error on θ introduces a large uncertainty on T. The result, as a whole, is probably not inconsistent with the temperature at the core boundary derived from the melting point of iron (see pp. 27–28).

CONVECTIVE EQUILIBRIUM IN THE MANTLE
THE ADIABATIC GRADIENT

The old idea of subcrustal currents [for a review of early work in this field see GUTENBERG (1939)] was investigated quantitatively by PEKERIS (1935) who found under plausible assumptions that relatively small differences in temperature might lead to convective motion at a rate of a few centimetres per year. SLICHTER (1941) pointed out that under convective conditions heat transfer in the mantle would be much greater than by conduction.

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The possibility that the mantle might be in convective, rather than in conductive, equilibrium leads to a method for estimating the temperature gradient which would be close to the adiabatic value, which is

$$\frac{dT}{dx} = \frac{\alpha g T}{c_P}$$

Knowledge of this gradient would be of interest as it would also represent the minimum initial gradient that is likely to exist under any theory of the formation of the earth. Even in an initially cold earth with no radioactive matter, self compression would lead to an adiabatic gradient, as pointed out by BENFIELD (1950).

Values of α and c_P are known for many minerals, but extrapolation to conditions obtaining in the deep mantle are hazardous, particularly with regard to α. VERHOOGEN (1951) showed that the ratio α/c_P could be obtained from seismic data, using DEBYE's theory of solids. His results are expressed in the form

$$\frac{c_P}{\alpha} = \frac{P}{\rho} + \frac{\phi}{m + \frac{1}{3}}$$

where m is an average value of $\frac{d \ln v}{d \ln \rho}$ for longitudinal and transverse elastic waves. Calculations require a knowledge of ρ, for which BULLEN's (BULLEN, 1947) values were adopted. Knowledge of the adiabatic gradient requires a knowledge of T, but one can form ratios of T_h/T_0 where T_0 is the temperature at some reference depth. VERHOOGEN finds by this method a ratio $T_{2600}/T_{200} = 1{\cdot}41$. A tentative and approximate temperature distribution in the mantle, based on the adiabatic gradient, was given in 1951 (TURNER & VERHOOGEN, 1951).

Similar calculations have since been carried out by UFFEN (1952) who obtained a ratio $T_{2600}/T_{200} = 1{\cdot}43$, and by VALLE (1950; 1952) who derived the relation

$$\frac{T^3}{v_p v_s^2} = \text{constant}$$

VALLE's ratio $T_{2600}/T_{200} = 1{\cdot}48$. All these calculations are based on BULLEN's density distribution, which may not be final, and on DEBYE's model of a solid

in which the number of lattice vibration modes with frequency in the range ν to $\nu + d\nu$ is proportional to ν^2; this model is presumably inadequate for complex structures. BIRCH (1952), using somewhat different methods, obtained the following values for the adiabatic gradient at various depths

depth (km)	0	800	2800
gradient (deg/km)	$0{\cdot}30q$	$0{\cdot}17q$	$0{\cdot}07q$

where $q = T \times 10^{-3}$. If we assume, for instance, $T_{2800} = 3 \times 10^3$ deg, the gradient at that depth is, according to BIRCH, 0·21°/km, as compared with 0·26°/km on VERHOOGEN's datum.

To find the adiabatic temperature at any depth from the adiabatic gradient, we still need to know the temperature at one point. This we might choose to be the bottom of the crust in continental areas. Estimates of the temperature there are very uncertain, as they depend on the assumed thickness of the crust and its average radioactivity; they range from 300° to 1000°. A value of 800°C = 1073°K might be fairly safe; and it would lead to an adiabatic temperature at the core boundary of 1700°K. The actual temperature at the core boundary is not likely to be less than this.

VERHOOGEN (1954) has suggested that an upper limit to the temperature at the core boundary could be obtained if one assumes that convection effectively occurs throughout the mantle. Lavas are erupted at the surface at a temperature which rarely exceeds 1200°C; from petrological arguments it is assumed that they form by partial melting of mantle material at a depth not much greater than 100 km and at temperatures not much greater than 1400°C. An adiabatic curve from this point reaches the core boundary at about 2500°C. This, it is argued, is the maximum permissible temperature at that depth, for if this temperature were exceeded, rising material which cools adiabatically as it rises would reach the level where it intersects the melting point curve at a temperature higher than 1400°, in which case the temperature of surface lavas would be greater than 1200°. Production of liquid magma is simply explained in the model as a consequence of convection and of the difference in slope of the adiabatic and melting-point curves; this is really ADAMS' argument on solidification of the earth in reverse.

It will be noted that in this model the average gradient in the mantle between crust and core [(2500–800)/2900 = 0·6°/km] is higher than the adiabatic value. The explanation is that the adiabatic gradient is really insufficient to start convection. This may be due in part to viscosity, as it is well known that convection in a viscous fluid requires a gradient greater than adiabatic. This effect is, however, very small. The main effect arises probably from the finite strength of the material forming the mantle, which will not begin to flow until the stresses exceed a certain value. No detailed calculations are available on the effects of finite strength on convective motion [see, however, BROOKS (1941)].

TEMPERATURE DETERMINATION FROM ELECTRICAL CONDUCTIVITY

The electrical conductivity σ of a dielectric substance increases rapidly with temperature, to which it is very sensitive. Knowledge of the electrical conductivity or its variation with depth in the mantle could thus be useful in determining the temperature or its gradient.

The electrical conductivity in parts of the mantle has been estimated by LAHIRI and PRICE (1939) from observed variations of the earth's magnetic field, particularly from the intensity ratio and phase difference of the internal and external components of the variations of the magnetic field for daily disturbances and storms. They conclude that the conductivity begins to increase rapidly downwards at a depth of the order of $0{\cdot}1R$ (R is the radius of the earth); the conductivity below this level is at least as high as 10^{-2} ohm^{-1} cm^{-1} (10^{-11} e.m.u.) and may continue to rise downwards to higher values. The conductivity at depths less than $0{\cdot}1R$ is affected by the possible influence of electrical currents induced in the oceans. Observations are compatible with the oceans having an effect equivalent to that of an ocean 1 km deep covering the whole earth. If the actual effects of the oceans are of this order, the conductivity below the surface down to $0{\cdot}1R$ must not be greater than 10^{-6} ohm^{-1} cm^{-1}. Similar calculations by RIKITAKE (1952) lead to a sudden increase in conductivity from 10^{-6} to 10^{-3} at 400 km depth.

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The conductivity of surface rocks is usually of the order of 10^{-6} to 10^{-9}; it strongly depends on porosity and water content. The conductivity of quartz at 500°C is 10^{-10}, parallel to the c-axis, and 10^{-12} perpendicular to this axis.

Neglecting impurity effects, the electrical conductivity of a dielectric may be represented by the relation

$$\sigma = \sigma_0 e^{-\varepsilon/kT} + \sigma_0' e^{-\varepsilon'/2kT}$$

where the first and second term represent respectively ionic and electronic contributions. σ_0 is usually of the order of 10^3 to 10^5 ohm^{-1} cm^{-1} for alkali halides but may be less for silicates. For intrinsic semiconductors σ_0' ranges usually from 30 to 3000 ohm^{-1} cm^{-1} [(MOTT & GURNEY, 1948), p. 158]. ε and ε', which are activation or excitation energies, may be of the order of a few electron-volts or 20–70,000 cal/mole.

RIKITAKE (1952) has attempted to deduce the temperature in the mantle from his conductivity distribution. He assumes the conductivity to be purely ionic and computes its dependence on pressure by making the dubious assumption that ε varies with volume in exactly the same way as lattice oscillation frequencies: $\dfrac{d \ln \varepsilon}{d \ln V} = \dfrac{d \ln \nu}{d \ln V} = -\gamma$, where γ is GRÜNEISEN's ratio. For a homogeneous mantle the jump in conductivity at 400 km depth must correspond to a temperature discontinuity, which is physically unlikely; one must assume a phase change at this depth. RIKITAKE takes σ_0 to be the same above and below the discontinuity. Starting from a temperature of 1080°K at 33 km depth, he obtains 1540°K at 400 km and 3170°K at 1600 km. A noteworthy feature of his result is that the temperature gradient steepens downward (see below).

As mentioned above, LAHIRI and PRICE find that the conductivity rises rapidly from 10^{-6} to 10^{-2} ohm^{-1} cm^{-1} at around $0{\cdot}1R$. The exact form of the conductivity-depth curve in this region cannot be inferred. The rise could be a sudden, discontinuous one, which is unlikely as present seismological evidence indicates no phase change or elastic discontinuity at that depth. LAHIRI and PRICE find that the slowest-varying function consistent with their data is of the form

$$\sigma = c_0 \left(\frac{r}{R}\right)^{-m} \qquad \ldots.(5)$$

where $c_0 = 4 \times 10^{-5}$ ohm^{-1} cm^{-1} and $m = 37$. We note that this relation cannot apply all the way to the core, as it would lead to an electrical conductivity at the core boundary $\left(\frac{r}{R} = 0{\cdot}545, \sigma = 2{\cdot}3\ 10^{+5}\right)$ far in excess of that (1–10 ohm^{-1} cm^{-1}) deduced by RUNCORN (1954) from the core-mantle coupling and the screening of the secular variation. We note also that a rise in electrical conductivity at a rate equal to, or greater than, that given by equation (5) must imply a change in the mechanism of conduction. This can be shown in the following way: let the conductivity be of the general form

$$\sigma = \sigma_0 e^{-\varepsilon/kT}. \qquad \ldots.(6)$$

We notice that for constant σ_0, σ increases with increasing T or decreasing ε. Eliminating σ between (5) and (6) and solving for T we get

$$T = \frac{\varepsilon}{k} \frac{1}{b + m \ln \left(\frac{r}{R}\right)}$$

where $b = \ln (\sigma_0/c_0)$. If ε and σ_0 are independent of r, the temperature gradient β is

$$\beta = -\frac{dT}{dr} = \frac{KmT^2}{\varepsilon r}$$

and β increases with depth, as in RIKITAKE's solution. This is improbable, as it would correspond physically either to a downward decrease in thermal conductivity, or to absorption of heat, the heat flux decreasing upward. If we retain a term $\frac{\partial \varepsilon}{\partial r}$ we find again that $\frac{\partial \beta}{\partial r} < 0$, irrespective of the sign and magnitude of $\frac{\partial \varepsilon}{\partial r}$. The condition $\frac{\partial \beta}{\partial r} > 0$ can only be satisfied if

$$-\frac{\partial^2 \varepsilon}{\partial r^2} > \frac{mK}{r}\left(2\beta + \frac{T}{r}\right).$$

Alternatively, if we assume ε constant but allow for a variation in σ_0, we find that the condition $\frac{\partial \beta}{\partial r} > 0$ requires $\frac{\partial^2 \sigma_0}{\partial r^2} \neq 0$. This means that either ε or σ_0, or both, much vary with depth at a rate such that their second derivatives with respect to r are not negligible. Notable changes in σ_0 and ε that are apparently not accompanied by sudden changes in other properties most probably indicate change from ionic to electronic conduction or vice versa. Since neither σ_0 nor ε nor their derivatives are known, the conductivity data around $0{\cdot}1R$ cannot be used to determine the temperature or its gradient.

Let us now turn to the lower part of the mantle, between 900 km and the core boundary. RUNCORN (1955) finds that in this region the average conductivity $\bar{\sigma}$ must be about 1 ohm^{-1} cm^{-1}; this result is based on a study of the sudden changes in the rate of the geomagnetic secular variation and on the mantle-core coupling required to explain observed changes in the length of the day. RUNCORN and TOZER (1955) have also shown, on the basis of HUGHES' (1953) measurements of the conductivity of olivine, that the conductivity in the deep mantle is most likely to be electronic. Assuming a linear temperature variation of the form

$$T = T_c(1 - \alpha L)$$

where L is height above the core boundary and T_c is the temperature at this boundary, and from the relation $\sigma = \sigma_0 \exp[-\varepsilon/2kT]$, a value of ε may be calculated for given values of T_c, α and σ_0 such that $\bar{\sigma} = 1$. For $\sigma_0 = 10$ ohm^{-1} cm^{-1}, RUNCORN (1955) obtains the following results:

α (10^{-8} cm)	T_c (deg K)	Average gradient αT_c (deg/km)	ε (eV)	σ_{900}	σ_c
0·1	2600	0·26	0·92	0·77	1·17
0·15	5200	0·78	1·80	0·4	1·2
0·3	10000	3·0	3·28	0·18	1·9

The excitation energy for intrinsic electronic conductivity in olivines and pyroxenes is, according to HUGHES (1953), about 3·2 eV in the range 600–1100°C at ordinary pressure. RUNCORN finds, from the change in ultra-violet absorption threshold under pressure, that ε will decrease at a rate of about 0·65 per cent per 10,000 atmos. If this value can be extrapolated to the pressure prevailing at the core boundary, ε at that depth would be about 1·3 eV. As the rapid change in conductivity between 600 and 900 km is probably to be attributed to a rapid decrease in ε, the actual value of ε in the lower mantle might even be less than 1·3. For $\alpha = 0{\cdot}1$ and $T_c = 3000$°K (average gradient = 0·3 deg/km), we find $\varepsilon = 1{\cdot}25$ eV for $\sigma_0 = 10$ ohm^{-1} cm^{-1} and $\varepsilon = 1{\cdot}04$ eV for $\sigma_0 = 6{\cdot}25$ ohm^{-1} cm^{-1}. The value of ε is thus rather sensitive to σ_0, the value of which can only be guessed by analogy with the behaviour of semi-conductors under ordinary pressure. Theoretically, σ_0 depends essentially on the electronic mobility which in turn is determined by interactions between thermal (elastic) lattice waves and the electron waves; it will be of the general form (KITTEL, 1953, p. 276).

$$\sigma_0 = \frac{A}{m} \frac{\rho^{1/3}\theta^2}{C^2}$$

where A is a numerical constant, m is the effective mass of an electron, ρ is the density of unit cells and θ is DEBYE's temperature; C is proportional to $\int[\text{grad } u]^2 \mathrm{d}V$, where u is the lattice potential function. As the gradient of u will be very sensitive to the lattice spacing, C^2 may increase faster than $\rho^{1/3}\theta^2$ and σ_0 may actually decrease with depth in the mantle.

It would thus seem that the electrical properties of the lower mantle are not inconsistent with a core boundary temperature of about 3000°K and an average gradient in the lower mantle of 0·3–0·5 deg/km; values of T_c higher than 5000° again seem to be ruled out. The rapid rise in conductivity between 600 and 900 km which, as we have seen, must correspond either to a rapid increase in σ_0 or a rapid decrease in ε, is most readily explained by assuming a phase change for which there is, however, no seismic evidence. Alternatively, it could result from a change from dominantly ionic to dominantly electronic conduction, ionic conduction being gradually suppressed by increasing pressure; this requires that ionic conduction should remain important to a greater depth than seems likely from RUNCORN and TOZER's calculations. It is most unlikely that this rapid change in conductivity should be an effect of temperature alone.

Electrical Conductivity in the Core

The existence of convective motion in the core and resultant electromagnetic effects suggests a low temperature of the order perhaps of that deduced from SIMON's data on the melting point of iron. If convective motion is to exist, the gradient must be greater than the adiabatic one; for a given rate of heat generation in the core, this condition sets an upper limit to the thermal conductivity. Indeed, if the thermal conductivity were sufficiently large, all heat could be carried away by conduction and convection would not occur. On the other hand, the electrical and magnetic effects associated with the convective motion require a fairly high electrical conductivity. Since the ratio k/σ in metallic conductors is proportional to T (Franz-Wiedemann law), a low value of k and a high value of σ necessarily imply a low value of T.

Numerical calculations are, however, extremely uncertain. The temperature gradient for convective instability of a rotating conducting fluid with a magnetic field impressed upon it may be very different from the adiabatic value (CHANDRASEKHAR 1953). Heat may be generated in the core by radioactivity, or by JOULE effects associated with electrical currents. The thermal conductivity that enters into the F.W. relation is the electronic term; the ratio of the latter to that arising from thermal agitation (phonon conductivity) is difficult to evaluate precisely. As noticed before, the adiabatic gradient is not exactly known, nor is the electrical conductivity. Any temperature calculation on this basis would thus be affected by an uncertainty factor of 2 or 3, at best.

CONCLUSIONS

Temperature estimates, such as those of HOLMES, ADAMS and JEFFREYS, that are based on a solution of the equation of heat conduction are unreliable; they depend on too many assumptions regarding the origin and early history of the earth, the values of the parameters involved, particularly the thermal conductivity, and the distribution of radioactive matter. There are reasons to doubt that heat transfer is mainly by conduction, as it is extremely difficult to reconcile at present heat flow measurements in continental and oceanic areas. One feels that such conjectural methods should not be used to determine temperature. When the temperature distribution will have been found by other means, these calculations may be used in reverse to infer the earth's history and constitution.

Methods for determining temperature by assuming convective equilibrium will be more reliable if it can be independently proven that convection does occur in the mantle. Pending such proof, the best available estimates to date appear to be those based on melting point data. If the core is assumed to consist of iron, there is little doubt that its temperature is of the order of 3000–4000°K; at any rate the temperature at the outer core boundary is less than 5000°K. Estimates based on solid state theory remain uncertain until more is known of the equation of state relevant to the mantle. It is interesting, however, to note the rather close agreement between estimates based on rather different methods (Table I); this agreement may, however, be fortuitous. Incidentally we note that a temperature of 3000°K at the core boundary is not consistent with an initially "hot" earth in conductive equilibrium; the appreciable cooling that in implied by the present low temperature requires a very high thermal conductivity, in agreement with UFFEN's findings, but which would lead to impossibly high

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Table I. Temperatures (degrees centigrade) within the Earth, as Estimated by Various Methods

Author	Date	Depth (km)										
		100	200	300	500	700	1000	1600	2900	5100	Centre	Remarks
HOLMES	1915	1575										Heat conduction equation.
ADAMS	1924	1300	1900	2400								Heat conduction equation.
JEFFREYS	1929	1100	1700	2100	2800	3400			10,000			Heat conduction equation. $T°$ at 2900 km is the assumed melting point at that depth.
GUTENBERG	1939	1500	1600	1700	1800	1900			ca. 2000			Assumes nearly adiabatic conditions below 100 km. Not based on detailed calculations.
DALY	1943	1200 at 70 km			2400		2900		4000			Based on assumed phase transitions and melting in upper mantle.
v. WOLFF	1943	1710° at 70 km 2660° at 120 km							3600		3900	Based on assumed phase transitions and melting in upper mantle. Adiabatic conditions in mantle.
TURNER and VERHOOGEN	1951	800–900							1500–2000			Adiabatic condition in mantle. Not based on detailed calculations.
UFFEN	1952								< 5000			Melting point, as determined from seismic data.
BIRCH	1952								< 10,000 5000°?			Seismic data. "A temperature of 5000° produces no serious discrepancy."

Table I (continued)

Author	Date	Depth (km)										
		100	200	300	500	700	1000	1600	2900	5100	Centre	Remarks
RIKITAKE	1952	900	1100	1200	1370	1570	1970	2900				Electrical conductivity. Phase transition at 400 km.
UREY	1952		2000		2700	"roughly adiabatic"						From assumed structure of mantle and melting point relationships.
SIMON	1953									3600 ± 200	< 3900	Melting point of iron.
MIKI	1954								5200–9800			Seismic data. Calculated for $\gamma = 1{\cdot}5$ and 2·0, and for mean atomic weight of 20 and 40. Calculations do not include the more probable case $\gamma = 1$.
JACOBS	1954								3300			From SIMON's melting point and JACOBS' adiabatic gradient in outer core.
UFFEN and MISENER	1954								$2700 < T < 5000$			Melting point of iron and of mantle material.
VERHOOGEN	1954	1000							$1500 < T < 2500$			Adiabatic gradient as determined from seismic data, and surface $t°$ of lavas.
	1955								< 2500			From thermal expansion.

surface heat flows. Methods of determining temperature from electrical conductivity are promising; but they require a more accurate knowledge of the electrical conductivity at depth and of the possible range of activation energies for the materials which form the mantle.

It is the reviewer's personal opinion that no inconsistencies arise at present from the assumption that the average gradient in the mantle is about 0·6°/km, the temperature at the core boundary being around 3000°K. Regional variations in temperature in the mantle may be expected.

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RADIOACTIVE METHODS FOR DETERMINING GEOLOGICAL AGE

By L. H. AHRENS

INTRODUCTION

THE extent to which radioactive methods for determining geological age had developed shortly before World War II is adequately described in HOLMES' (1937) readable "Age of the Earth". Research remained more or less in abeyance during the war years but has progressed impressively since and here an attempt will be made to survey progress during the post-war period. The general field has, however, developed so extensively that it will be difficult to review progress in all aspects and at the outset it will be necessary to define fairly specifically what will be covered. The selection of topics is somewhat arbitrary and is dictated partly by the author's familiarity with the topic and partly whether it is well suited for review: omission of a discussion of an age method or of some specific aspect should not be taken to imply lack of significance.

We will begin with the lead method—the first of the classical methods—which as a single method is the most highly developed and continues to develop vigorously. The helium method, the second of the classical methods, will be passed over. No other method has perhaps, had so many ups and downs and its present status is not clear and easily reviewed.* We pass next to two recent methods (strontium and argon) just coming into application and after reviewing the prospects of some potential methods ($K^{40} \rightarrow Ca^{40}$; natural fission and others) go on to a brief discussion of recent progress on the determination of meteorite ages. The final section gives references only to recent papers on (i) methods for determining the ages of ocean sediments, (ii) the use of photographic techniques for estimating age and (iii) indirect age methods—cube edge variation, radiation damage etc. The use of induced activity in C^{14} for archaeological dating will not be discussed.

Recent publications (RANKAMA, 1954; FAUL, 1954) on the significance of radioactivity to geology include detailed discussions of most of the radioactive methods for determining geological age. Accounts of several age methods may also be found in BULLARD and WILSON (1954) and KOHMAN and SAITO (1954).

THE LEAD METHOD

Analytical

A most significant single development has been the introduction of mass spectrographic methods (NIER, 1939; NIER *et al*, 1941) in place of laborious atomic weight determinations for estimating the proportion of radiogenic lead. The isotope information so provided has led to the possibility of calculating

* The He method has recently been thoroughly and authoritatively discussed by HURLEY (1954) who includes most of the early observations and traces the development of this method up to its present state.

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age by means of each specific parent: daughter ratio $\left(\frac{Pb^{206}}{U^{238}}, \frac{Pb^{207}}{U^{235}}, \frac{Pb^{208}}{Th^{232}}\right)$ as well as by means of the ratio $\frac{Pb^{207*}}{Pb^{206}}$ which also is time sensitive because of the differing half-lives of the respective parents ($U^{235} = 7{\cdot}1 \times 10^8$ years; $U^{238} = 4{\cdot}5 \times 10^9$ years). Use may also be made of the Pb^{206}/Pb^{210} ratio; this is a very recent development and is discussed separately later. The old chemical $\frac{Pb}{U + Th}$ age determinations have now been largely replaced by those based on specific parent: daughter isotope ratios; some workers carry out complete analyses (chemical and isotope) whereas others have been inclined to rely on $\frac{207}{206}$ only on the grounds that this ratio provides the most valid estimate of age. This assumption is controversial and we come back to it later after considering further progress in the development of analytical methods.

Refinement of mass spectrographic procedure itself has progressed impressively. The accuracy achieved by NIER and others who first used mass spectrographic procedures for age research was high and adequate for the purpose and later developments have been mainly in the direction of sensitivity and broadening scope of application. COLLINS *et al.* (1951; 1954) and DIBELER and MOHLER (1951) chose to employ Pb tetramethyl, a gas, in place of PbI_2 used by NIER and co-workers and claim advantages of speed and absence of memory effect. Other Pb compounds have been used successfully. FARQUHAR *et al.* (1953) compared results obtained from solid (PbI_2 and $PbCl_2$) and gas (Pb tetramethyl) samples and report satisfactory agreement. The combined use of the mass spectrograph with isotope dilution procedures, has been particularly striking. As an example, TILTON *et al.* (1952) and TILTON (1954) have been able to determine thorium down to ~ 1 μg quantities and to within $\sim 1\frac{1}{2}$ per cent, using a mass spectrograph—isotope dilution procedure with Th^{230} as carrier. This development is highly significant as many of the earlier Th determinations seem to be seriously in error and it now becomes possible to determine thorium precisely in accessory minerals such as zicron (see for example, Carnegie Institution, 1954). Microgram quantities of lead have also been determined mass spectrometrically (HESS *et al.*, 1953). The use of combined mass spectrographic—isotope dilution procedures may be compared with an equally effective application for the strontium and argon methods (see below).

Several other analytical procedures have been introduced for geological age research. HOLMES and SMALES (1948) successfully employed a polarographic procedure for the determination of total lead and uranium in monazite; the same worker (SMALES, 1952) has developed a procedure for the determination of low uranium concentrations in rocks and minerals by activation in the Harwell pile: a similar procedure for thorium is described by JENKINS (1954). LARSEN and co-workers (1952; 1953, and unpublished) used spectrochemical methods of analysis (see particularly WARING and WORTHING, 1953) for the determination of lead in zircon down to concentrations of a few parts per million; that is, concentrations of lead which are likely to be found in zircons as young as about

* Abbreviations $\frac{206}{238}$, $\frac{207}{235}$, $\frac{208}{232}$ and $\frac{207}{206}$ will be used hereafter.

20×10^6 years. A similar general procedure has been used by workers at M.I.T. (AHRENS and co-workers, unpublished) and is being employed elsewhere. Fluorimetric and colorimetric procedures for determining uranium in minerals and rocks are described by ADAMS and MAECK (1954).

Various sensitive procedures have been developed by DALTON and co-workers for the determination of the low concentrations of uranium and thorium usually

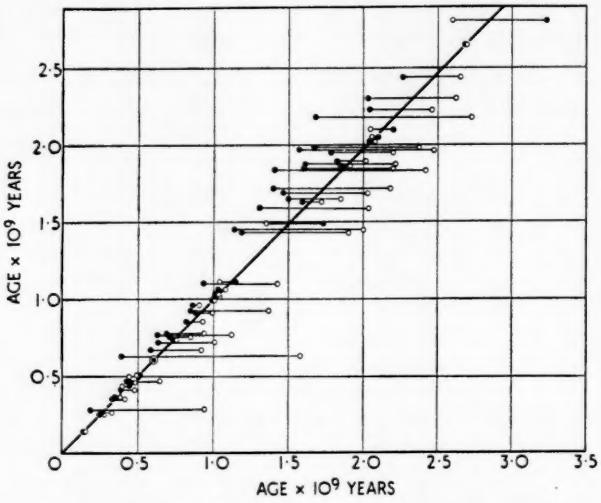

Fig. 1. Lead ages $\left(\frac{207}{235}, \frac{206}{238}\right.$ and $\left.\frac{207}{206}\right)$ of some 53 specimens. For the majority of the specimens the distribution is $\frac{207}{206} > \frac{207}{235} > \frac{206}{238}$; a few (about 1 in 5–10) show $\frac{206}{238} > \frac{207}{235} > \frac{207}{206}$ (Data mainly from FAUL, 1954).

present in meteorites: alpha counting of radon and thoron from chemically concentrated radium (DALTON *et al.*, 1953); counting of thorium C + C′ alphas in thorium B separated from chemically isolated thorium (DALTON *et al.*, 1953; 1954); fluorimetric determinations of chemically isolated uranium (DALTON *et al.*, 1953; 1954). The accuracy of the uranium determination is improved by the addition of U^{233} as tracer (DALTON *et al.*, 1954). PATTERSON *et al.* (1953) developed an isotope dilution—mass spectrometric procedure using enriched U^{235} as carrier (see also HESS *et al.*, 1953).

Although attention has been focused on the introduction of various sensitive analytical procedures we should not overlook the fact that wet methods of chemical analysis still serve satisfactorily for the determination of U, Th and total Pb when present at comparatively high concentrations, as in many uraninites for example.

To sum up, the development of analytical procedures has been most satisfactory (under favourable conditions, analytical error should not exceed ~ 1 per

cent (KULP *et al.*, 1954)), and although further investigations are naturally required, a lot of what requires to be done is much a matter of detail. We pass now to review the central problem of the lead method which is not in nearly so satisfactory a state; namely, lead age distribution—its nature and its cause.

Lead Age Distributions

Despite very accurate analytical measurements it is often difficult to estimate lead ages satisfactorily, particularly those of great age, because of internal disagreement. Although various age distributions have been observed, a fairly high proportion of all specimens show the distribution $\frac{207}{206}$ (age) $> \frac{207}{235} > \frac{206}{238}$; $\frac{208}{232}$ ages are quite often the lowest of all. Age distributions are shown in Fig. 1 (data from FAUL, 1954) which relates $\frac{207}{235}$ (ordinate) vs. $\frac{206}{238}$ and $\frac{207}{206}$. $\frac{208}{232}$ ages have been omitted because a high proportion are undoubtedly inaccurate due to analytical error and uncertainty of isotope correction; some $\frac{208}{232}$ ages are referred to again later.

Gain or loss of parent or daughter is the usually suggested cause for internal age disagreement (see for example HOLMES, 1948) and on this assumption attempts are often made to manipulate data so as to bring about agreement. WICKMAN (1942) suggested that loss of emanation might take place, but that this loss, however, would be confined to radon as its half-life (3·825 days) was far greater than that of thoron (54·5 sec) and actinon (3·92 sec). He drew attention to the observations of FÖYN (1938) who demonstrated that emanation from bröggerite increased steeply with decrease in particle size. WICKMAN also mentioned the effect of recoil energy on path distance travelled by emanation in a crystal. Radon diffusion loss is frequently regarded as the principal cause for internal disagreement and several authors (HOLMES, (several papers); KULP *et al.*, 1954; LOUW, 1954) have calculated ages on this basis. On this basis also, KULP *et al.* (1954) recommend the $\frac{207}{235}$ age as the most precise single lead age estimate as it is not influenced by radon loss whereas $\frac{206}{238}$ is depressed and $\frac{207}{206}$ elevated. They give measured indications of the magnitude of emanation loss and report that samarkites lose $< 0{\cdot}1$ per cent Rn and that uraninites and pitchblendes lose 0·1 to 10 per cent; secondary minerals such as carnotite may lose 20 per cent or higher. The majority of 15 recently analysed Witwatersrand uraninites and thucholites show an age distribution of $\frac{207}{206} > \frac{207}{235} > \frac{206}{238}$ (LOUW 1954). These authors attribute the cause mainly to Rn diffusion loss and calculate that such losses may be as high as ~ 20 per cent or so. HORNE and DAVIDSON (1955), however, report laboratory observations on Witwatersrand uraninite which indicate that radon diffusion loss is insignificant. Further (indirect) evidence that radon loss is not the cause

Table I. "Age" Calculations of the most primitive monazites and uraninites

Specimens and locality	Age ($\times 10^6$ years)				
	$\frac{206}{238}$	$\frac{207}{235}$	$\frac{208}{232}$	$\frac{207}{206}$	Convergent
Monazite, Ebonite Tantalum Claims, Bikita District, S. Rhodesia	2675	2680	2645	2680	2680
Monazite, Jack Tin Claims, north of Salisbury, S. Rhodesia	2260	2470	1940	2650	2680
Monazite, Irumi Hills, N. Rhodesia	2040	2330	1390	2620	2680
Monazite, Antsirabe, Madagascar	1400	1850	610	2420	2680
Monazite, Huron Claim pegmatite, southeast Manitoba	3217	2839	1827	2590	—
Uraninite, Huron Claim pegmatite, southeast Manitoba	1564	1985	1273	2475	2680
Uraninite, Dominion Reefs, Klerksdorp, Transvaal	1678	2200	3672	2730	> 2680

of the common $\frac{207}{206} > \frac{207}{235} > \frac{207}{238} \gg \left(\frac{208}{232}\right)$ age distribution comes from the ages of Rhodesian monazite (HOLMES, 1954). Geological considerations as well as the discussion below indicate that the ages of the Rhodesian monazites are the same. $\frac{207}{235}$, $\frac{206}{238}$, $\frac{207}{206}$ and $\frac{208}{232}$ ages of one specimen agree well (Table 1) and

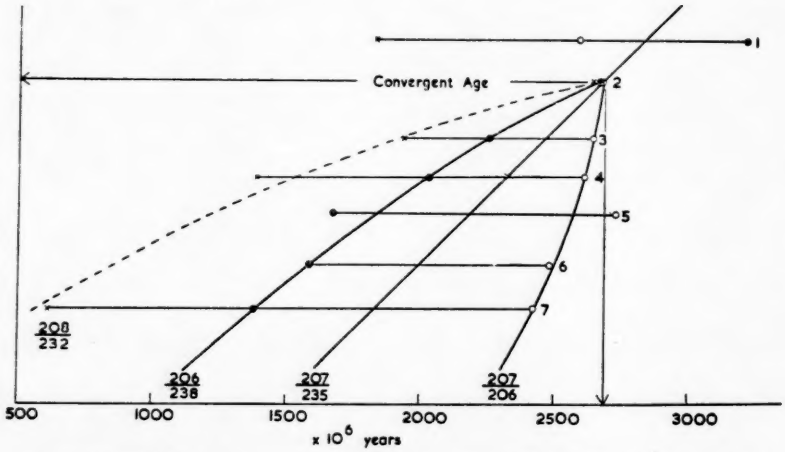

Fig. 2. The Rhodesia age pattern. 1—monazite, Huron Claim, Manitoba; 2, 3, and 4—monazite, Rhodesia (Bikita, Salisbury and Irumi, respectively); 5—uraninite, Klerksdorp, Transvaal; 6—uraninite, Huron Claim, Manitoba; 7—monazite, Antsirabe, Madagascar. Varying lead deficiency is one suggested cause of the development of this pattern.

it is reasonable to assume that this age is precisely known; the others diverge as indicated in Table 1 and particularly in Fig. 2 (adapted from AHRENS, 1955a).

If radon loss were the cause of the age distribution, the $\frac{207}{235}$ ages should have remained the same, whereas they do not and the whole age array may be conveniently explained on the basis of varying lead deficiency (AHRENS, 1955a and b)—see also HOLMES (1954). Fig. 2 shows also that the age distributions of Manitoban uraninite (but not the Manitoban monazite, which is qualitatively distinct) and Madagascan monazite fit an extension of the Rhodesia pattern precisely, consequently indicating that their age distributions are caused by lead deficiency as well. AHRENS (1955a) concludes that the ages of each of the five participants of the Rhodesia pattern are *precisely* the same, namely 2680×10^6 years. (General support of similarity of age of some of the specimens has come from strontium age determinations of lepidolite (AHRENS, 1949; AHRENS and MACGREGOR, 1951; DAVIS and ALDRICH, 1953; NICOLAYSEN *et al.*, 1953; NICOLAYSEN, 1954). It is concluded further (AHRENS, 1955a) that age distributions which are qualitatively similar to those participating in the Rhodesia pattern (i.e., $\frac{207}{206} > \frac{207}{235} > \frac{206}{238}$ see Fig. 1 for example) are also due to lead deficiency and not to loss of 206 only as a result of Rn diffusion loss. If so $\frac{207}{206}$ measurements are the most valid single lead age estimates—at least of pre-Cambrian minerals—as suggested by NIER (1939) and COLLINS *et al.* (1954); see also comments by BULLARD and WILSON (1954). If, however, the convergent age is the true lead age, $\frac{207}{206}$ estimates must as a rule be regarded as slight underestimates—see Fig. 2 and AHRENS (1955a).*

When considering comparatively young specimens, $\frac{207}{206}$ measurements tend to be less reliable (KOHMAN and SAITO, 1954) as the ratio becomes less sensitive to age change and may be subject to a very large error indeed because of uncertainty of the constitution of igneous lead; this has been the experience of STIEFF *et al.* (1953) in their investigations on uranium ores from the Colorado plateau. It should be recalled also that the ratio $\frac{207}{206}$ is more sensitive to mass spectrometric error than are the other ratios (KULP *et al.*, 1954).

Cause of Assumed Lead Deficiency

Deficiency of lead could be due to loss of lead itself or escape of some intermediate member of a decay chain. Loss of lead is usually considered to be caused either by leaching as in an obviously weathered mineral, or by some process of mineralization or re-working of the mineral. It has recently been pointed out, however, (AHRENS, 1955a and 1955b) that the high degree of order

Note added in proof

* KULP and ECKELMAN (*Bull. Geol. Soc. Am.*, (1955), **66**, 767) have also reached the conclusion that individual age estimates, including $\frac{207}{206}$ are underestimates. These authors assume lead loss (of comments below) in place of radon loss which Kulp and co-workers had previously regarded as the cause of internal disagreement.

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in the Rhodesia pattern (Fig. 2) points to physical control of lead deficiency as neither leaching nor re-working are likely to produce so much order. Escape of emanation could be such a physical process but no simple relationship between either emanation half-life or recoil energy and the lead deficiency order of 208 (greatest deficiency) > 207 > 206 has been found (AHRENS, 1955b). The deficiency order (207 > 206) is the reverse of that indicated by the age relationship, $\frac{207}{235} > \frac{206}{283}$, and is apparently due to the fact that the half-life of U^{235} is much less than that of U^{238}—for detailed discussion, see AHRENS (1955b). In this paper it is pointed out that no satisfactory solution to the actual cause of apparent lead deficiency has yet been found and that the very high order of the Rhodesia pattern could be interpreted to indicate that some other process, rather than one of escape, might have taken place.

Expansion of the Lead Method

(i) *Accessory minerals from igneous rocks*—A great step forward in the use of radioactive methods in geology has been the expansion of the application of the lead method to accessory minerals of common igneous rocks. This opens up vast new possibilities as the lead method is no more confined for the most part to pegmatites.

The accessory zircon, as well as sphene, apatite and some complex rare earth minerals, including monazite, are the principal hosts to U and Th in igneous rocks. A favourable feature about these minerals is that although their structures readily accept U (+ Th), presumably as U^{4+} and Th^{4+}, they tend to reject entry Pb^{2+} mainly because its size and charge are unsuitable. As a result, it has been possible to employ rapid methods without isotope analysis control as well as refined procedures based on complete analyses. LARSEN *et al.* (1952 and 1953) were the first to publish a set of ages based on the rapid procedure; these determinations have since augmented by many others and some eighty-five are listed by FAUL (1954). A thick source count is made of total activity and total lead is determined, as for example by a spectrochemical procedure (WARING and WORTHING 1953). An approximate age is obtained from the relationship,

$$t = \frac{k\text{Pb}}{\alpha}$$

where t is age, Pb total lead, α the thick source count and k a constant which is 2600 for U alone and 1990 for Th alone. In zircon, activity is due essentially to U. It should be recalled that chemical ages $\left(\frac{\text{total Pb}}{\text{U} + \text{Th}}\right)$ are often low* in uraninite and monazite and that Pb/α ages are likely therefore also to be underestimates, particularly in the pre-Cambrian.

* It was once thought that such chemical ages tended to be over-estimates, as allowance could not be made for the presence of common lead; it now seems likely, however, that they are under-estimates (AHRENS, 1955b) as lead deficiency appears to be very common—see above. In fact, as an extreme example, we have monazite from Antsirabe, Madagascar (for complete data, see HOLMES and CAHEN, 1955) which has a chemical age of $\sim 700 \times 10^5$ years; that is, $\sim \frac{1}{4}$ of its likely age of 2680×10^6 years (see Fig. 2).

Precise measurements based on individual parent/daughter ratios have been attempted (see for example, Carnegie Institution, 1954). Very few observations have been made, but it seems that in zircon also, the Pb age distribution appears to be $\frac{207}{206} > \frac{207}{235} > \frac{206}{238} > \frac{208}{232}$. For example, zircon separated from granite (Cape Town, South Africa) was found to have $\frac{207}{206}$ (550×10^6 years), $\frac{206}{238}$ (347×10^6 years) and $\frac{208}{232}$ (278×10^6 years)—Carnegie Institution (1954). This

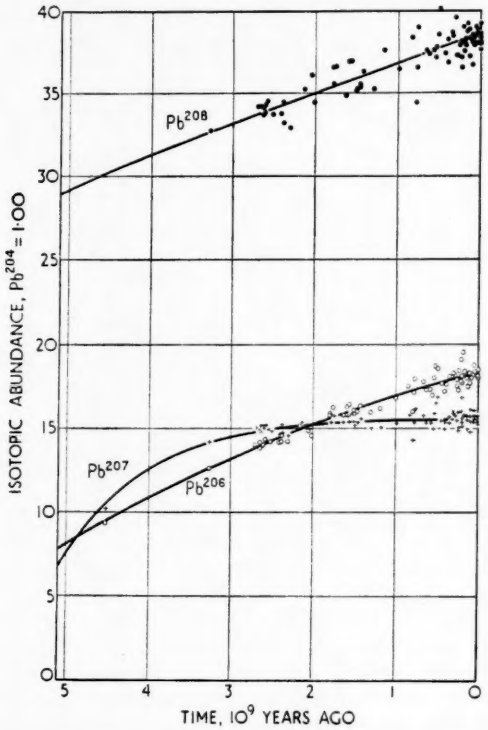

Fig. 3. Variation of isotope composition of lead from galena of different ages. Roughly two-thirds of all known measurements have been used; others are regarded as anomalous. (After FAUL, 1954. With kind permission of John Wiley & Sons.)

disagreement may at first sight appear highly unsatisfactory. It seems quite possible, however, that a convergent type estimate (AHRENS, 1955a) could be made provided several specimens were analysed.

As the accessories usually occur in low abundance, a considerable bulk of rock (often several pounds) is required. Concentration of zircon, etc. may be achieved by the combined use of heavy liquids, magnetic separator and flotation cells—see for example, FAIRBAIRN (1954).

(ii) *Lead ores*—The first isotope analyses of galena (NIER, 1938) indicated that with few exceptions, isotope constitution tended to vary regularly with age.

Use has been made of this type of regularity for estimating the age of the earth* (GERLING, 1942; KOCZY, 1943; HOLMES, 1946; HOLMES, 1947; HOUTERMANS, 1947; BULLARD and STANLEY, 1949; VINOGRADOV *et al.*, 1952; COLLINS *et al.*, 1953; ALLAN, 1955). RUSSELL *et al.* (1954) have developed the idea that such regularities could also be made for dating lead ores. Fig. 3 (after FAUL, 1954) shows the nature of these regularities and serves to provide some impression of the accuracy with which individual ages may be made. It should be emphasized, however, that only two thirds of all published analyses have been employed in Fig. 3, the others being regarded as anomalous.

The use of galena would, of course, expand the scope of the lead method enormously. It is quite clear, however, that although single galena ages may serve as useful guides, too much reliance cannot be placed on them as precise

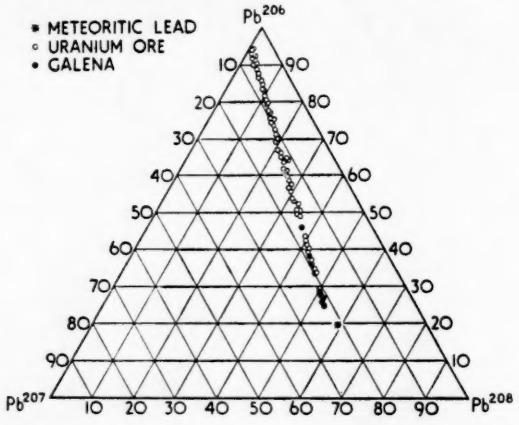

Fig. 4. Isotope variation of lead in uranium ores (O) and galena (O) from Colorado plateau. Note overlap and also the location of the point for lead from Canyon Diablo meteorite. (After FAUL, 1954. With kind permission of John Wiley & Sons.)

estimates. In general, the validity of a galena age estimate tends to increase with age (see Fig. 3) and estimates less than $\sim 800 \times 10^6$ years are not attempted (BULLARD and WILSON, 1954). If suites of specimens from the same area give the same age, it seems reasonable to assume that a reliable estimate has been made. Most published galena ages may be found in BULLARD and WILSON (1954) and WILSON *et al.* (1954).

The relationship (Fig. 4—after CAMERON in FAUL, 1954) between Pb^{206}, Pb^{207} and Pb^{208} in a suite of galenas and uranium ores from the Colorado plateau is most instructive for several aspects of the lead method. Although the galena constitutions concentrate toward the one end of the regularity, there is considerable overlap into the uranium ore range which is quite extensive. The location of the point for the Canyon Diablo meteorite (PATTERSON, 1955 and earlier papers) is neatly placed at the end of the regularity; the isotope constitution of this lead is presumed to be that of true primary lead—that is, the constitution of lead when originally formed and not modified since by additions

* "Earth" is used loosely here and original papers should be consulted about what actual event authors are considering.

from the radioactivity of uranium and thorium. For further data in this respect, see PATTERSON (1955).

Use of the Ratio $\frac{206}{210}$

It is theoretically possible to employ the ratio of any one of the members of a decay series to that of a stable daughter provided the series is in equilibrium; hence ratios such as $\frac{Pb^{206}}{Ra^{226}}$, $\frac{Pb^{206}}{Po^{214}}$ and $\frac{Pb^{206}}{Pb^{210}}$ are possibilities in addition to those already discussed. Practical application, however, is only possible provided that the half-life is not too short and chemical purification not unduly difficult. HOUTERMANS (1951) suggested the use of $\frac{Pb^{206}}{Pb^{210}}$. A test on pitchblende of known age from Belgian Congo appeared successful (BEGEMANN *et al.*, 1953 and earlier papers) and a fairly thorough investigation (KULP *et al.*, 1953) on ten specimens of uraninite, pitchblende and samarskite, all of assumed known age, seems to have firmly established the usefulness of this ratio. Many details of analytical procedure are described by KULP *et al.* (1953). Analytical manipulations are simplified to some extent as all measurements are confined to lead as both Pb^{210} and Pb^{206} determinations are made on the same sample.

BULLARD and WILSON (1954) sum up the advantages of the Pb^{210} method as follows:

> "(1) The ratio may be determined on any fraction of the total lead in the mineral and hence, it is unnecessary to carry out a quantitative chemical analysis. The proportion of Pb^{206} present in a specimen of radiogenic lead is determined by a mass spectrometer. (2) Pb^{210} has a half-life of about 22 years and is easily measured by radioactive counting methods, although the amount would always be too small to measure mass spectrochemically. (3) The danger of contamination is slight since lead can be readily separated by chemical means from other members of the radioactive family. In addition the $\frac{Pb^{206}}{Pb^{210}}$ ratio is unaffected by recent loss of uranium and only slightly affected by radon loss if the loss has been nearly uniform throughout the life of the mineral."

Pb^{210} measurements should turn out to be very useful in providing a clue to the cause of the discrepant specific parent: daughter ages (see above).

METHODS BASED ON THE RADIOACTIVITY OF THE ALKALI METALS K AND Rb

Although radioactivity was observed in K and Rb some fifty years ago, its application to the determination of geological age is a comparatively recent development. The simple nature of the decay $\left(K^{40} \overset{\beta}{\nearrow} Ca^{40}\ ;\ Rb^{87} \xrightarrow{\beta^-} Sr^{87}\right)$,

in each case with insignificant recoil effect, is a particularly desirable feature; moreover, two of the daughter elements (Sr and Ca) are not seriously "foreign" to the host mineral structures and are not likely to escape. From fundamental considerations, the alkali-metal methods are superior to the lead method, but we shall see as we come to each in turn that progress has nevertheless been slowed by various other considerations—analytical accuracy and uncertainty of decay constants, for example. We will trace progress in the strontium method first, as it is the oldest of the alkali metal methods, then consider the argon method and finally survey the prospects of a potential calcium method together with other potential direct methods.

The Strontium Method

As in the case of K^{40}, the decay constant of Rb^{87} has been the subject of much investigation. Emission of a soft β has been a main cause of difficulty of accurate determination of half-life; various estimates, arranged in chronological order, are given in Table 2.

Table II. Half-Life Determinations of Rb^{87}.

Source	*Half-life* ($\times 10^6$ years)
HAHN and ROTHENBACH (1919)	7·5
MÜHLOFF (1930)	12·0
ORBAIN (1931)	4·4
STRASSMANN and WALLING* (1938)	6·3
CHAUDHURY (1942)	7·5
EKLUND (1946)	5·8
HAXEL, HOUTERMANS and KEMMERICH (1948)	6·0
CURRAN, DIXON and WILSON (1952)	6·15
LEWIS (1952)	5·9
MCGREGOR and WIEDENBECK (1952)	6·4
BÄHNISH, HUSTER and WALCHER (1952)	4·8 (lower limit)
MCGREGOR and WIEDENBECK (1954)	6·2
FLINTA and EKLUND (1954)	6·1

The possibility that bound β-decay may be of some significance in this respect is mentioned by KOHMAN (1954).

The first strontium age determinations (HAHN and WALLING, 1938) was discussed shortly after the discovery (HAHN *et al.*, 1937) of radiogenic strontium in lepidolite, the mineral which has the highest rubidium concentration. In some of the first investigations, rubidium was determined by a flame photometric procedure, total strontium by a combined chemical enrichment—spectrochemical procedure (HYBBINETTE, 1943) and the proportion of radiogenic strontium by a mass spectrographic analysis (photographic recording) of $SrBr_2$ (MATTAUCH, 1947).

AHRENS (1947; 1949) sought to develop a rapid optical spectrochemical procedure for direct determination of $\frac{\text{Sr (total)}}{\text{Rb}}$ ratios in lepidolite. Some thirty specimens have been examined this way and although the procedure serves

* Indirect. Based on Pb age of $1{\cdot}99 \times 10^9$ years for southeast Manitoba pegmatite; using a convergent Pb age value of 2680×10^6 years (AHRENS, 1955a) would increase this value.

very satisfactorily for reconnaissance and in this respect has revealed a second area containing uniquely old pegmatites (AHRENS and MACGREGOR, 1951) accuracy is nevertheless unsatisfactory for many purposes. A marked step forward, as in many age methods, has been the introduction of isotope-dilution—mass spectrochemical procedures (DAVIS and ALDRICH, 1953; TOMLINSON and DAS GUPTA, 1953). For strontium, ALDRICH and co-workers have used Sr^{84} as the spike whereas TOMLINSON and DAS GUPTA chose Sr^{90}. Such procedures require only an extremely small quantity of specimen and accuracy is claimed to be high. A few of the first determinations are evidently in error but have since been revised (see discussion by AHRENS, 1955c). Most application of the strontium method has thus far been made in the pre-Cambrian (see for example, NICOLAYSEN *et al.*, 1953; NICOLAYSEN, 1954) and it is here that this method evidently will find its greatest application.

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SCHREINER, JAMIESON and SCHONLAND (1955) report ages on three distinct varieties of mica (purple bi-axial, $2{\cdot}69 \times 10^9$ years; green bi-axial, $2{\cdot}82 \times 10^9$ years and purple uniaxial, $2{\cdot}57 \times 10^9$ years) from a single hand specimen from the Popes Claim pegmatite, Salisbury, S. Rhodesia. Although the three ages agree in magnitude, the difference is significant and greater than analytical error. This illustrates a source of error not heretofore observed, the cause of which, however, is yet to be found. The magnitude of $2{\cdot}7 \times 10^9$ years (average of the above values) is somewhat lower than that reported by NICOLAYSEN *et al.* (1953) and NICOLAYSEN (1954) who used a similar analytical procedure and is very close to the convergent lead age (Table I) for Rhodesia pegmatites.

Strontium ages are, as a rule, higher than those obtained by the lead method. It has been customary to accept the lead age scale as correct and seek some cause of error (half-life of Rb^{87} for example) for the discrepant Sr ages. AHRENS (1955b) finds evidence from the Rhodesia age pattern (Fig. 2) and other observations, however, which may be taken to indicate that the Pb age scale might possibly be seriously in error—at least at great ages—and that the strontium age scale may be closer to the true geological time scale.

As in the lead method, there has been some progress toward expanding the strontium method. Lepidolite and other Rb-rich minerals are confined to pegmatites. AHRENS (1949), WHITING (1951) and HOLYK (1952) have suggested and discussed the possibilities of using biotite, a common rock forming mineral, and TOMLINSON and DAS GUPTA (1953) report one actual determination. Whereas $>$ 90 per cent of the strontium from lepidolites and $> \sim 40$ per cent of the strontium from pollucite, amazonite, hydrothermal microcline and some pegmatitic micas is radiogenic, the proportion in biotite from igneous rocks is much lower, usually 1 to 10 per cent (ALDRICH *et al.*, 1953; AHRENS, 1954). Nevertheless this proportion of radiogenic strontium is significantly high and it should be possible to determine strontium ages of quite a high proportion of pre-Cambrian biotites.

The Argon Method

No other method, perhaps, shows indications of greater promise than does the argon method. It is too early yet to attempt a definite prediction, but available data must be regarded as very encouraging when due allowance is given to the usual allotment of teething troubles associated with the development of a new method.

Shortly after ALDRICH and NIER (1948) demonstrated the presence of appreciable quantities of radiogenic A^{40} in some potassium minerals, SMITS and GENTNER (1950) attempted some age determinations of oligocene sylvine (Rhine Valley). Their paper describes the determination of total argon as well as its mass spectrometric analysis. Later papers (GENTNER, PRÄG and SMITS, 1953; GENTNER, GOEBEL and PRÄG, 1954) discuss the dependence of argon diffusion on size of KCl crystals. Although these applications to salt deposits are indeed of use, it is in the dating of igneous rocks that the argon method seems to hold greatest promise; here it may be applied to the most ubiquitous of all minerals, mica and feldspar. Before surveying progress in this direction, it would be as well to recall that some uncertainty still exists about the precise values of the decay constants of K^{40}, the rarest isotope of potassium (0·0119 per cent, NIER, 1950; 0·0118 per cent, REUTERSWARD, 1952). The β^- decay constant appears to be fairly accurately known ($\lambda = 0{\cdot}55 \times 10^{-9}$ years^{-1}; BIRCH, 1951; BURCH, 1953) but the value of the branching ratio is less certain and values based on direct laboratory measurements are usually higher than those based on the determination of radiogenic A^{40} in minerals of assumed known age. Table III summarizes most of this information.

Table III. Branching Ratio (λ_e/λ_β) for K^{40}

Source	λ_e/λ_β
(1) KÖHLHORSTER (1930)	0·061
(1) MÜHLHOFF (1930)	0·040
(3) BĚHOUNEK (1931)	0·16
(4) GRAY and TARRANT (1934)	0·02
(5) AHRENS and EVANS (1948)	0·112
(6) GRÅF (1948)	0·115 ± 0·025
(7) HESS and ROLL (1948)	0·109
(8) HIRZEL and WAFFLER (1948)	0·087 ± 0·012
(9) FLOYD and BORST (1949)	0·05 ± 0·01
(10) SAWYER and WIEDENBECK (1949)	0·098 ± 0·010
(11) FAUST (1950)	0·122 ± 0·014
(12) HOUTERMANS, HAXEL and HEINTZ (1950)	0·105 ± 0·010
(13) SMALLER, MAY and FREEDMAN (1950)	0·05 ± 0·01
(14) SPIERS (1950)	0·102
(15) BURCH (1953)	0·119 ± 0·006
(16) LIBBY (1954)	0·10
(17) SHILLIBEER *et al.* (1954)	0·09
(18) WASSERBURG and HAYDEN (1955)	0·085
(19) SUTTLE and LIBBY (In Press)	0.10

Most values claimed to be within ~ 10 per cent. 1 to 16, based on direct observation, 17 and 18, indirect (see above). MOUSOF (1952) and RUSSELL *et al.* (1953) had previously reported a value of 0·06, but subsequent argon measurements caused an increase of this value.

Although cognizance must be taken of some uncertainty in the decay constants of K^{40}, it seems reasonable to assume that this difficulty is being resolved, and we pass now to survey progress of application of the argon method to dating igneous rocks. The first such attempt is that of GERLING *et al.* (1952a) who obtained nine argon ages (mainly on microcline) and who reported satisfactory agreement between argon ages and those of associated minerals determined by the lead and helium methods. Subsequent publications from two

groups (Chicago—WASSERBURG and HAYDEN (1954); Toronto—SHILLIBEER *et al.* (1954)) also indicate satisfactory agreement between lead and argon ages provided some adjustment is made to the observed branching ratio (Table III). The recent paper by WASSERBURG and HAYDEN (1955) contains considerable analytical detail and using the isotope dilution technique which they describe it is apparently possible to determine ages as low as $\sim 20 \times 10^6$ years. This is most satisfactory. The proportion of radiogenic A^{40} is usually > 95 per cent in feldspar: this high proportion reduces the magnitude of error which could have been caused by uncertainty of isotope constitution of primary argon. The close relationship between lead age and argon age have lead WASSERBURG and HAYDEN (1955) to conclude that argon diffusion is probably insignificant. This is not surprising as recoil effects are insignificant and although argon is a large atom, it presumably occupies a site previously occupied by the large K^+ (1·33A) and hence might not cause undue strain in the structure particularly as the ratio $\frac{\text{A atoms}}{\text{K ions}}$ is never large.

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The determination of potassium presents no serious problem, unless present at low concentrations as in meteorites (see AHRENS, PINSON and KEARNS, 1952; EDWARDS and UREY, 1955, in this respect) and Lawrence-Smith fusion or flame photometric methods provide satisfactory accuracy.

FLEMING and THODE (1953a) draw attention to one possible cause of error in the argon method; namely the great variation of A^{36}/A^{38} ratios in highly active minerals. Age measurements usually involve A^{40}/A^{36} measurements and if the mineral happened to be near a highly active one, the "normal" A^{36} abundance may be disturbed.

Potential Methods

In addition to natural radioactivities already referred to, several others are known; Table IV lists most of those. (U, Th, K and Rb are included for the sake of completion). A few other radioactive elements have been reported; for example, V^{50} ($> 10^{12}$ years) $\rightarrow Cr^{50}$?; Ti^{50}?; Sb^{123} (very long) $\rightarrow Te^{123}$; I^{129} ($1{\cdot}72 \times 10^7$ years) $\rightarrow Xe^{129}$; Nd^{150} (2×10^{15} years?) $\rightarrow Pm^{150}$. Natural fission (spontaneous and neutron-induced) is discussed separately—see p. 58. Each radioactivity represents a potential age method and prospects of their use in this respect wll be surveyed briefly.

Most values from General Electric Chart of Nuclides (4th Edition—1952); Sm^{147} (BEARD and WIEDENBECK, 1954); Re^{187} (HERR, HINTENBERGER and VOSHAGE, 1954); La^{138} (MULHOLLAND and KOHMAN, 1952). See KOHMAN and SAITO (1954) for a discussion of these decays.

The first criterion which must be considered is that of half-life: if too long, the daughter concentration becomes so low that it is impossible to measure. What this lower limit is, is impossible to predict as the introduction of newer sensitive procedures keeps on lowering detection limits. For a start we will regard half-lives greater than about $\times$ 100 to 1000 the age of early pre-Cambrian rocks ($\sim \times 10^9$ years) as an approximate limit. This rules out Te^{130} ($\sim 10^{21}$ years), Bi^{209} (10^{17} years), In^{115} (6×10^{14} years) and Sm^{147} (10^{16} years). Of the remaining decays, that of $K^{40} \rightarrow Ca^{40}$ will be considered first.

Radiogenic Ca^{40} was discovered (INGHRAM *et al.*, 1950) in sylvite, and as in the argon method, calcium ages of sylvite may presumably be made. Whereas,

however, the argon method appears capable of wide application for dating igneous rocks, the potential calcium method would be very restricted. This is due to swamping of small quantities of radiogenic calcium in almost all igneous minerals. The problem has been discussed by AHRENS (1951) who concludes that only lepidolites as well perhaps as some other late pegmatitic mica and feldspar could be used. Most lepidolites contain about 10 to 500 ppm total

Table IV. Examples of Natural Radioactivity

	Decay		*Half-life (years)*
U^{238} (99·28%)	complex	Pb^{206}	$4{\cdot}5 \times 10^{9}$
U^{235} (0·71%)	complex	Pb^{207}	$7{\cdot}1 \times 10^{8}$
Th^{232} (100%)	complex	Pb^{208}	$1{\cdot}39 \times 10^{10}$
K^{40} (0·012%)	e	A^{40}	
	β^-	Ca^{40}	$1{\cdot}33 \times 10^{9}$ (see Table 3)
Rb^{87} (27·85%)	β^-	Sr^{87}	6×10^{10} (see Table 2)
In^{115} (95·77%)	β^-	Sn^{115}	6×10^{14}
Te^{130} (34·49%)	double β^-	Xe^{130}	$\sim 10^{21}$
La^{138} (0·089%)	e	Ba^{138}	
	β^-	Ce^{138}	$\sim 7 \times 10^{10}$
Lu^{176} (2·6%)	e	Yb^{176}	
	β^-	Hf^{176}	$2{\cdot}4 \times 10^{10}$
Re^{187} (62·93%)	β^-	Os^{187}	$\sim 5 \times 10^{10}$
Sm^{147} (15·1%)	α	Nd^{143}	$1{\cdot}25 \times 10^{16}$
Bi^{209} (100%)	α	Tl^{205}	$2{\cdot}7 \times 10^{17}$

calcium (AHRENS, 1951; HOLYK, 1952) and calculation based on the potassium and calcium (total) content of lepidolites of assumed known age indicate that up to $\sim$ 30 per cent of the calcium of pre-Cambrian lepidolites may be radiogenic. Potassium is easily determined in lepidolite by conventional methods and HOLYK (1952) describes a spectrochemical procedure for determining total calcium; a mass spectrometric analysis may be made using the $\frac{Ca^{40}}{Ca^{44}}$ ratio. Despite several investigations which have been undertaken to detect radiogenic Ca^{40} in lepidolite, none have yet apparently been successful.

Although the calcium method is restricted in scope, a calcium age of a strontium + argon dated lepidolite would be invaluable as it would serve as a triple age and also a check on the branching ratio (λ_e/λ_β) of K^{40}.

The next shortest half-life is probably that of Lu^{176}. This is a fairly rare isotope (2·6 per cent) and as lutetium is an extremely rare rare-earth, the amount of daughter produced is very small. A rare-earth mineral containing 1 per cent Lu would produce about 0·1 ppm total daughter elements in $\sim 10^9$ years. Of this about two thirds would be Yb^{176} (this isotope is 12·73 per cent of natural Yb). The abundance of ytterbium is usually far greater than lutetium in rare-earth minerals and this seems to make the determination of radiogenic Yb^{176} virtually impossible. Hf^{176} offers slightly better possibilities because the total hafnium concentration in a rare earth mineral may be low enough to permit a determination of radiogenic Hf^{176}: the operation would in any event be difficult. Similar concentration magnitudes have to be considered for the decay $La^{138} \rightarrow Ce^{138} + Ba^{138}$. As cerium is a common rare-earth, this seems to rule out the possibility of using the ratio $\frac{La^{138}}{Ce^{138}}$. SAITO *et al.* (1954) have looked for Ba^{138} in old rare-earth minerals but were unsuccessful.

Although rhenium and osmium do not show close geochemical coherence, as compared with the rare-earth elements, for example, rhenium is unfortunately extremely rare and rarely reaches an effectively high concentration; a maximum of $\sim$0·3 per cent is reached in some molybdenites. LIBBY (1954—in KOHMAN and SAITO, 1954) has discussed the possibility of using this mineral and finds cause for some optimism. A generally favourable feature is that common osmium contains only 1·64 per cent Os^{187}. HINTENBERGER *et al.* (1954) have recently provided the necessary experimental evidence to indicate that an osmium method is a real possibility. They found 16 ppm total Os (99·5 per cent radiogenic) in a rhenium rich (0·32 per cent Re) molybdenite. Two analytical methods were used for Os: one an isotope dilution procedure involving the addition of cyclotron irradiated Os and the other a spectro-photometric procedure using thio-urea complex of Os. Total parent was determined by a colorimetric method (BEESTON and LEWIS, 1953) and a neutron activation method. Further observations on the Re^{187}/Os^{187} ratios in molybdenite are awaited with much interest.

Natural fission is another possible age method. Its discovery goes back to 1940 (FLEROV and PETRZHAK, 1940a and b) and since then strong evidence (KHLOPIN, GERLING and BARANOVSKAYA, 1947; MACNAMARA and THODE, 1950; FLEMING and THODE, 1953b; WETHERILL, 1953) indicating two types of natural fission has been provided; spontaneous fission of U^{238} ($t_{\frac{1}{2}} = 3{\cdot}1 \times 10^{15}$ years POSE, 1943); $8{\cdot}04 \times 10^{15}$ years (SEGRÉ, 1945); $1{\cdot}3 \times 10^{16}$ years (PERFILOV, 1947); $1{\cdot}9 \times 10^{15}$ years (YAGODA and KAPLAN, 1949) and neutron induced fission in U^{235} ($t_{\frac{1}{2}} = 1{\cdot}87 \times 10^{17}$ years (SEABORG, 1951)). It is evident that natural fission half-lives are extremely long and hence extremely small quantities of stable fission products are produced. Nevertheless measureable amounts of fission-product Xe and Kr have been quantitatively determined in highly active minerals (MACNAMARA and THODE, 1950; FLEMING and THODE, 1953b and WETHERILL, 1953) and from the point of view of use for age measurements, FLEMING and THODE state, "A quantitative measure of the amount of fission gas present in ores per gram of uranium and a knowledge of the proportion of spontaneous fission that has occurred should make age calculations possible."

See also THODE (1954—in FAUL, 1954) in this respect. MARBLE and YAGODA (1952—in MARBLE, 1952) have mentioned that trace quantities of rare earths might be produced by natural fission in U + Th minerals. Until such time that all known processes of natural fission (spontaneous and induced) are properly understood and more observations are at hand, it will not be possible to predict with confidence what likelihood there is of a successful application of natural fission for determining geological age. There is also the problem of possible unobserved fission processes. For example, PEPPARD *et al.* (1952) find U^{233}/U^{238} ratios of $1{\cdot}3 \times 10^{-13}$ to 4×10^{-11} in pitchblende and monazite, respectively, and the presence of U^{233} could be attributed to the reaction Th^{232} $(n\gamma)$ Th^{233}; $Th^{233} \xrightarrow{\beta^-} Pa^{233} \xrightarrow{\beta^-} U^{233} \longrightarrow Tl^{205}$. There are other possibilities.

BRIEF SURVEY OF RECENT INVESTIGATIONS ON THE AGES OF METEORITES

Earlier attempts, mainly by Paneth and co-workers, to determine the ages of meteorites were based on the helium method; see for example, ARROL, JACOBI and PANETH (1942). These observations were confined for the most part to metal meteorites and indicated a very wide age range. The recent observations of PANETH, REASBECK and MAYNE (1952; 1953) on He^3/He^4 ratios in meteorites has necessitated some re-evaluation. It is found, however, (PANETH, 1954, for example) that although these considerations do influence the He calculations, many iron meteorite ages remain comparatively young (most 100 to 200×10^6 years, a few down to 1×10^6 years); that is, when compared with the ages of the oldest rocks and the argon and lead ages (see below) of meteorites. For further discussion of these discrepancies, see UREY (1955).

GERLING and PAVLOVA (1951) found an argon age of 3×10^9 years for two chrondrites (see also GERLING and RIK, 1952b). The potassium content which they reported was considerably higher than that typical of chrondrites (AHRENS, PINSON and KEARNS, 1952; EDWARDS and UREY, 1955) and from this consideration their age is an under-estimate. WASSERBURG and HAYDEN (1955) found argon ages of $4{\cdot}0$ to $4{\cdot}5 \times 10^9$ years for two chondrites, using a λ_e/λ_β branching ratio of 0·09. This magnitude is slightly less than that (two at $\sim 3{\cdot}5 \times 10^9$ years, one at $1{\cdot}8 \times 10^9$ years) reported since by THOMSON and MAYNE (1955). These workers used a branching ratio of 0·13 and a decrease in the value of this ratio to 0·09 would bring their age estimates closer into line with those of WASSERBURG and HAYDEN (1955).

These age magnitudes of ~ 4 to 5×10^9 years are in remarkably good agreement with lead age estimates reported by PATTERSON (1955). (This paper gives references to earlier observations). Although such agreement may in many respects appear most satisfactory and may indicate the correct age magnitude for meteorites they should still be viewed with great caution until many further data become available. It should be recalled that these magnitudes agree generally with estimates of the age of the oldest rocks, the earth, the elements, solar system and universe—see for example, AHRENS (1955c). In contrast to these great ages, the estimated argon ages of tectites (SUESS *et al.*, 1951; GERLING and YASCHENKO, 1952) are only 10^6 to 10^7 years. GERLING and YASCHENKO regard this as evidence against a cosmic origin for tectites.

SELECTED REFERENCES ON METHODS AND TECHNIQUES NOT DISCUSSED

Helium Method

HURLEY (1954). As this recent paper is exhaustive and gives complete literature coverage, no further references need be given.

Dating of Ocean Sediments (Radium and Ionium Methods).

URRY, (1941, 1942; 1948a and b; 1949); PIGGOT and URRY (1942); KULP and CARR (1952); VOLCHOK and KULP (1952); PETTERSSON (1951; 1954); KRÖLL (1954); PICCIOTTO and WILGAIN (1954); HOUGH (1953); HOLLAND and KULP (1954a and b); ISAAC and PICCIOTTO (1953).

Use of Photographic Emulsion for Age Determinations

(i) as applied to Pb^{210} method: SÖDING (1951); WILGAIN (1953) and HOUTERMANS (1954).

(ii) as applied to pleochroic haloes: HAYASE (1954); HOUTERMANS (1954), and DEUTSCH, HIRSCHBERG and PICCIOTTO (1954).

The photographic emulsion has also been most effectively employed for obtaining information about the distribution of α-activity in rocks. This information is particularly instructive for the development of the lead method. Some recent significant contributions are: CURIE (1946); HEE (1948; 1954); PICCIOTTO (1949; 1950; 1952); YAGODA (1949); COPPENS (1951 and 1952); COPPENS and COPPENS (1950) and FORD (1951). For further references, see RANKAMA (1954).

Indirect methods for Determining Geological Age

(i) Cube edge—WASSERSTEIN (1951; 1954); BROOKER and NUFFIELD (1952).
(ii) Radiation damage—HOLLAND and KULP (1950); HOLLAND (1954); HURLEY and FAIRBAIRN (1952).

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SEISMOLOGY AND THE BROAD STRUCTURE OF THE EARTH'S INTERIOR

By K. E. BULLEN

1. INTRODUCTION

THE present chapter is a summary of a course of lectures given by the author in the University of Cambridge during the Michaelmas Term of 1954. The primary purpose is to show how, during the last twenty years or so, seismology has been a principal source of ideas on the structure of the Earth's deep interior, and especially on the variation of density, compressibility and pressure. Only a limited section of seismology needs to be discussed for this purpose, namely work on bodily seismic waves and on travel-time tables. There will be little reference to many vigorously active fields of seismology such as near-earthquake and explosion studies, and work on surface waves, seismicity, microseismology and conditions near earthquake foci.

When an earthquake occurs, waves issue from a confined region below the Earth's outside surface, called the focus. The time during which the main energy is released usually does not exceed the order of a second or so, except possibly in extreme earthquakes. In a great earthquake, the energy released is of the order of 10^{25} ergs. The linear dimensions of the focal region may be of the order of several kilometres. In the formal part of the following account, the focus will be treated as a point source, and it will be assumed that the energy is released at the focus at an instant of time. Deviations from these artificial conditions have of course to be considered when seismograms are being interpreted. In large earthquakes, bodily seismic waves spread through the entire interior of the Earth, including the centre. The waves emerge again at the outer surface, and are recorded at the world's six hundred seismological observatories (JEFFREYS, 1951). The seismograms traced at these observatories are the raw material from which important features of the Earth's internal structure can be inferred.

In constructing a theory from which to interpret the records, the Earth is treated, to a first approximation, as a perfectly elastic, isotropic body, and the infinitesimal strain theory is used in considering the transmission of the seismic waves. Deviations from this first-order theory have to be examined, but it transpires that none of these deviations is important in relation to the broad inferences to be made in the present chapter. For the ideal Earth which it is thus sufficient to consider, the elastic behaviour is fully described in terms of just two parameters, in addition to the density ρ. The two parameters will be selected as the incompressibility or bulk-modulus k (the reciprocal of the compressibility) and the rigidity μ, these parameters being of more direct physical significance than alternative parameters that have sometimes been employed.

The terms "solid" and "fluid" will be used quite often in the following pages. Sometimes concern is expressed at the use of such terms at pressures of the order of a million atmospheres which hold in the Earth's deep interior. In this

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chapter, it is to be understood that, if a material is described as solid, then its elastic behaviour conforms, to good approximation, to the set of equations

$$p_{ij} = (k - \tfrac{2}{3}\mu)\theta\delta_{ij} + 2\mu e_{ij} \qquad \ldots.(1)$$

which apply to (perfectly elastic, etc.) solids in ordinary laboratory conditions. In (1), the p_{ij} and the e_{ij} are components of stress and strain, respectively, θ is the dilatation (equal to Σe_{ii}), and δ_{ij} is the Kronecker delta; k and μ enter as coefficients in this set of equations. For a material to be called solid it is also assumed that the magnitudes of k and μ are both at least say 10^{11} dyn/cm^2. When the term fluid is used, exactly the same is to be understood, except that μ is small, say less than 10^{10} dyn/cm^2. It is to be appreciated of course that the "solids" and "fluids" of this context are, by virtue of the ideal theory assumed in the preceding paragraph, free from such actual complications as imperfections of elasticity, including viscosity. As already stated, the ideal, first-approximation, theory serves to indicate the broad variation of ρ, k and μ in the Earth's interior. An indication of the possible order of magnitude of the effects of imperfect elasticity and of aeolotropy is given in work of JEFFREYS (1952) Section 2.04 and STONELEY (1949).

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By introducing the deviatoric stress and strain tensors P_{ij} and E_{ij}, defined by

$$p_{ij} = P_{ij} + \tfrac{1}{3}(\Sigma p_{kk})\delta_{ij}$$
$$e_{ij} = E_{ij} + \tfrac{1}{3}(\Sigma e_{kk})\delta_{ij},$$

it is possible (BULLEN, 1953a, Section 2.5) to re-write (1) as

$$\tfrac{1}{3}(\Sigma p_{kk}) = k\theta \qquad \ldots.(2)$$

$$P_{ij} = 2\mu E_{ij}, \qquad \ldots.(3)$$

where the parameters k and μ appear in separate equations.

In a solid material to which stress-strain relations of the form (1) (or (2) and (3)) apply it is readily deduced (BULLEN, 1953a, Section 4.1) that the material can transmit two types of bodily waves, the primary or P waves which are dilatational (or compressional), and the secondary or S waves which are rotational. The speeds α and β of the P and S waves are given by

$$\alpha^2 = \frac{k + \frac{4}{3}\mu}{\rho} \qquad \ldots.(4)$$

$$\beta^2 = \frac{\mu}{\rho}. \qquad \ldots.(5)$$

If the material is fluid, so that μ may in practice be neglected, we have

$$k = \rho\alpha^2; \quad \beta = 0. \qquad \ldots.(6)$$

The circumstances of seismic wave transmission are such that k and μ are adiabatic parameters. It needs to be remarked that, in the formal derivation of (4) and (5), the density ρ and the parameters k and μ are treated as constants. In the Earth, ρ, k and μ all vary with depth, but it happens that the variation is sufficiently small over one seismic wave-length to justify the neglect of this variation to a first approximation in the above derivation.

2. SEISMIC TRAVEL-TIME TABLES

A seismogram may show many bodily wave phases, each phase corresponding to a particular route of a ray from an earthquake focus to the recording station, many routes being possible because of reflection at the Earth's outer surface and reflection and refraction in the interior. (In seismology, as in optics, the energy can for many purposes be regarded as being transmitted along rays.) Also there are distinct phases according as particular segments of the path of a ray are traversed in the *P* or *S* wave type. Each phase usually appears on the seismogram as a group of waves, and seismograms contain information on the times of onset, the amplitudes and periods of these waves. By far the most precise information about the Earth's interior has to date come from the arrival-time data—measurements of the times of onset—and it is this data chiefly which will be used in the following discussion.

From the arrival-time data, it is possible to compute the travel-times, from focus to recording station, for many phases and over all angular distances. The problem is not an easy one since the latitude, longitude, the depth of the focus and the time of origin of every earthquake considered are initially unknown. Tables of these travel-times have been evolved from crude beginnings, starting from near the beginning of the present century.

The tables of ZÖPPRITZ of Göttingen as adapted by TURNER of Oxford were used in preparing the International Seismological Summary up to the end of the year 1929. But between 1925 and 1928, it had come to be suspected that there were large errors in these tables, exceeding 20 sec even in the case of tables for the main *P* phase.

A number of seismologists had used arrival-time data from one or two or a relatively small number of earthquakes to suggest improvements to the tables. But in 1928 JEFFREYS came to the conclusion that a major revision was necessary, combining the observations of all the best-recorded earthquakes as summarized in the I.S.S., and he embarked on a long research to evolve better tables. The writer of this article had the privilege of being associated with JEFFREYS in various aspects of this work over the period 1931–39. The ensuing travel-time tables, referred to as the J.-B. tables (JEFFREYS & BULLEN, 1940), have been used in compiling the I.S.S. for earthquakes since December 1936. (A preliminary version of the J.-B. tables was used in the I.S.S. for earthquakes over the period 1930–36.)

The J.-B. tables relate to a standard model Earth which is spherically symmetrical and such that each internal spherical surface of equal velocity encloses the same volume as the corresponding level surface in the actual Earth. Allowances for the Earth's ellipticity are applied in the form of separate tables (JEFFREYS, 1935; BULLEN, 1937b–39). Other sources of deviation from spherical symmetry, such as differences in the outer layering between continental and oceanic regions, are not allowed for, since there is as yet insufficient detailed knowledge available for the purpose. Thus the J.-B. tables apply, in a certain sense, to "average" earthquakes. The discussions in the following sections of this chapter will relate to the symmetrical Earth model as above defined. Thus, for any given phase, the travel-time T between a pair of points of the outside surface will be regarded as depending only the angular distance Δ subtended at the centre and not on the location of a focus or observing station.

Over the period 1933–39, GUTENBERG and RICHTER (1934–39) made independent revisions of the extant seismic travel-times, and they also used large quantities of arrival-time data. Although their methods of treating the data were rather different from those used in deriving the J.-B. tables, the two sets of results were in general in good agreement. The greatest differences were less than one-tenth of the greatest corrections that had to be applied to the ZÖPPRITZ-TURNER tables.

The precision of the seismic travel-time tables had now reached the point where the tables could be applied to investigating the Earth's interior in much more detail than had been possible hitherto. In particular, T was known as a numerical function of Δ within an accuracy of 1 to 2 sec for all Δ in the case of

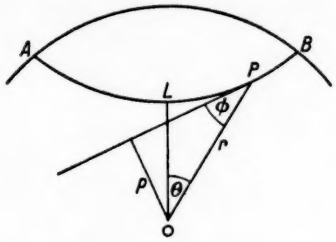

Fig. 1

the main P rays. The same applied to S rays for $0° \leqslant \Delta \leqslant 105°$, except that the uncertainties were a little greater. The numerical results to follow are based on the J.-B. tables, but the work of GUTENBERG and RICHTER will be used to indicate degrees of uncertainty in inferences; it may be assumed that where the two sets of results are noticeably different, there is greater uncertainty in the conclusions that may be drawn than elsewhere.

3. INFERRING THE P AND S VELOCITY DISTRIBUTIONS

From the travel-time data, it is possible, subject to certain restrictions which will be discussed a little later, to infer the P velocity distribution throughout the Earth, and the S velocity distribution throughout the mantle (i.e. down to a depth of 2900 km). The essential method was evolved by HERGLOTZ (1907) and BATEMAN (1910) some forty-five years ago, and has since been refined by others.

Let $ALPB$ be a seismic ray as shown in Fig. 1, A and B being terminal points at the outside surface, P any point of the ray, and L the lowest point. Let r, θ be the polar coordinates of P referred to the Earth's centre O, and let p be the perpendicular from O to the tangent at P. Let v be the (P or S) wave velocity at P.

As in the optical case, FERMAT's principle is relevant, so that the travel-time T along $ALPB$ is stationary. This leads (BULLEN, 1953a, Section 6.1; BULLEN, 1954b, p. 83) to the Snell's-law relation

$$\frac{r \sin \phi}{v} = \lambda,$$

i.e.
$$\frac{p}{v} = \lambda, \qquad \ldots.(7)$$

where the parameter λ is constant along an assigned ray, but will vary from ray to ray. (FERMAT's principle incidentally requires the whole ray *ALPB* to be in the plane *AOB*.) By considering a pair of neighbouring rays, it can be shown (BULLEN, 1953a, Section 7.21) that

$$\lambda = \frac{dT}{d\Delta}. \qquad \ldots.(8)$$

For the ray *ALPB*, Δ is equal to $2\int d\theta$, the integration ranging from *L* to *B*. Since

$$\frac{d\theta}{dr} = \frac{p}{r\sqrt{(r^2 - p^2)}},$$

we then have, using (7) and introducing η defined by

$$\eta = \frac{r}{v}, \qquad \ldots.(9)$$

$$\Delta = 2\int_{\lambda}^{\eta_0} \frac{\lambda}{r\sqrt{(\eta^2 - \lambda^2)}} \frac{dr}{d\eta}\, d\eta, \qquad \ldots.(10)$$

where the subscript zero is being used to denote values which variables take at the Earth's outside surface. The lower terminal of the integral in (10) is λ since $\eta = r/v = p/v$ at *L*, and $p/v = \lambda$ by (7).

Now, if v were known as a function of r, then r would be a known function of η, and Δ could therefore by (10) be determined for any assigned value of λ. By (8), it thus follows that if the *P* or *S* velocity distributions were known, the corresponding T-Δ relations could be deduced using (10).

Our problem is the inverse of this, namely, given the T-Δ relation, to deduce the v-r relation; and it involves solving (10) as an integral equation. (Actually (10) is a particular form of ABEL's integral equation.) The simplest method of solving (10), that of RASCH (JEFFREYS, 1939b), is to apply the operation

$$\int_{\eta_1}^{\eta_0} \frac{d\lambda}{\sqrt{(\lambda^2 - \eta_1^2)}}$$

to both sides of (10), where η_1 is any suitably selected value of η. This operation involves integrating over a family of rays between the highest for which $\Delta = 0$ and the lowest for which $\Delta = \Delta_1$, say. On carrying out the operation, and simplifying, the result is found (BULLEN, 1953a, Section 7.4) to be

$$\int_0^{\Delta_1} \cosh^{-1}\left(\frac{\lambda}{\eta_1}\right) d\Delta = \pi \log\left(\frac{r_0}{r_1}\right), \qquad \ldots.(11)$$

where r_1 corresponds to η_1.

Suppose a value of η_1 is assigned. Then, since

$$\eta_1 = \lambda_{\Delta=\Delta_1} = \left(\frac{dT}{d\Delta}\right)_{\Delta_1},$$

the corresponding value of Δ_1 can be derived from the travel-time tables. Also, λ is known as a function of Δ from the travel-time tables. Thus, by (11), r_1 is determined for the given η_1. By carrying out a series of such (numerical) integrations, r is determined as a function of η; hence v is determined as a function of r.

In general the velocity increases with increase of depth in the Earth for both P and S waves. But if there are ranges of depth in which v decreases with increase of depth at such a rate that

$$\frac{dv}{dr} - \frac{v}{r} > 0, \qquad \ldots.(12)$$

then the method fails when such ranges are included in the integration. This is because the left-hand side of (12) is proportional to $d\eta/dr$, and a change of sign of $d\eta/dr$ in the range of integration causes the integral in (10) to diverge. The failure occurs for an obvious physical reason in that, at a level where (12) applies, the downward curvature of a ray (BULLEN, 1954b, p. 87) is found to exceed the curvature of the level surface itself, so that no ray can have its lowest point at such a level and the velocity distribution cannot be uniquely determined.

It transpires that, in the Earth, possible occurrences of the condition (12), although they add to uncertainties in the final results, are sufficiently limited to enable the velocity distributions to be fairly well-determined; some of the complications will be referred to in Section 4.

It may be remarked that the presence of an internal surface of discontinuity across which v decreases by a finite amount from above to below would likewise involve failure of the method. This case occurs with the P velocity at the boundary between the mantle and core, and if only P observations were available it would not be possible to infer the P velocity distribution in the core. This particular difficulty is surmounted using the travel-times for the phase *SKS* (where S here applies to S rays in the mantle, and K to a P ray in the core), the S velocity in the lower mantle being less than the P velocity in the core.

It needs to be remarked further that, even when the HERGLOTZ-BATEMAN equation can be validly employed, there are certain types of velocity variation in which the uncertainties in the determination may be specially high. For example, an abnormally high rate of increase of velocity with depth is associated with triplication of the travel-times for given Δ, and there are consequent uncertainties in practice in the complete form of the travel-time curve; and this leads to increased uncertainty in the computed velocity results. These and other abnormal features (BULLEN, 1953a, Sections 7.31–7.38) all occur in the Earth, and the net result is that the velocities are more certainly determined for some ranges of depth than for others. From the point of view of inferring the Earth's internal structure, it is fortunate that the "difficult" ranges of depth are relatively few and limited in extent.

4. DIVISION OF THE EARTH'S INTERIOR INTO REGIONS

In 1939, JEFFREYS (1939b, c) computed values of the P velocity α throughout the Earth, and of the S velocity β down to a depth of 2900 km, using the J.-B. travel-times. This led to a division of the Earth, with respect to depth, into several regions, each characterized by the type of velocity variation in it. The nomenclature *A*, *B*, *C*, *D*, *E*, *F* and *G* to denote the regions was introduced in

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the course of subsequent work (BULLEN, 1940; 1942) on the problem of the Earth's density variation. At a later stage (BULLEN, 1949a), it appeared that the lowest 200 km of the region *D* were sufficiently different in a significant physical respect from the rest of *D* to warrant the subdivision of *D* into the regions *D′* and *D″*. Table I summarizes the velocity distributions in these layers.

Table I. Regions of the Earth's Interior

Region	Range of depth (km)	*P* velocity (km/sec)	*S* velocity (km/sec)
A	0–33	(Widely varying)	(Widely varying)
B	33–410	7·8–9·0	4·4–5·0
C	410–1000	9·0–11·4	5·0–6·4
D′	1000–2700	11·4–13·6	6·4–7·3
D″	2700–2900	13·6	7·3
E	2900–4980	8·1–10·4	(Not observed)
F	4980–5120	10·4–9·5	(Not observed)
G	5120–6370	11·2–11·3	(Not observed)

Various features of the velocity distributions in the regions *A* to *G* will now be discussed in some detail, and the discussion will include a consideration of uncertainties and of additional evidence since 1939.

Region A

In continental regions, seismic arrival-times indicate the presence of a discontinuity at a depth of 30 to 35 km below the outside surface. (The depth appears to be 50 per cent or more greater in the vicinity of certain mountain ranges.) The discontinuity has been called the Mohorovičić discontinuity because of work of A. MOHOROVIČIĆ on a 1909 Croatian earthquake. There is some evidence that the discontinuity may be fairly sharp, and some seismologists have lately claimed to have detected seismic waves reflected upwards from it. The depth of the discontinuity is much less than 30 km in oceanic regions, and some seismologists have given depths as little as 5 km below the ocean floor.

The region *A*, extending from the outside surface to the Mohorovičić discontinuity, is often called the "crust" or "crustal layers." The use of the term crust is of course purely conventional, since it can no longer be held that the material below is of less rigidity.

Details of the velocity variations in the crust are at present highly controversial among seismologists (BULLEN, 1954b, Chapter VI). But it is clear that the changes in both *P* and *S* velocities are far more complicated inside the region *A* than in any other of the regions listed in Table I. In calculations involving the Earth's deeper interior, the crust has been conventionally taken to consist of a layer 15 km thick and of density 2·65 g/cm^3, resting on a second layer 18 km thick and of density 2·87 g/cm^3. This model is now out-of-date, but, because there is as yet no final crustal picture in sight, there are advantages in keeping to this model for standard comparison purposes in calculations relating to the whole Earth. Errors in the adopted model are of minor consequence in results applying to the deep interior.

Region B

From the J.–B. tables, it had appeared that the P and S velocities increase with depth, starting from a value of 7·8 km/sec. in the case of the P velocity just below the Mohorovičić discontinuity, at a very uniform rate to a depth near 410 km. This is the region B of Table I.

Since 1939, additional evidence has made it clear that the value of 7·8 km/sec needs to be raised to about 8·1 km/sec in most regions. GUTENBERG (1948) considers that the P and S velocities diminish with increase of depth in the uppermost 100 km or so of the region B, the rate of diminution being such that the relation (12) applies; if this proves to be the case the velocity distribution inside B becomes considerably uncertain. GUTENBERG postulates minimum P and S velocities at a depth near 140 km, and his most recent velocity values below this depth differ from those in Table I in having rather steeper gradients in the region B. On the most recent work of JEFFREYS (1954), the travel-times for P are almost proportional to the angular distance Δ for $0° < \Delta < 15°$ (neglecting crustal layer complications); this implies a diminution of velocity with depth just short that involved in the condition (12).

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In these circumstances, it is evident that more work needs to be done before there is secure knowledge of the velocity variation in the region B. The velocity values themselves are not likely to need corrections much exceeding 0·3 km/sec, the major uncertainty being in the form of the variation of the velocity gradients.

Region C

The boundary between the regions B, C is associated with the "20° discontinuity", a bend in the travel-time curve against Δ to which BYERLY (1926) had drawn attention in the case of P waves in 1926. The bend was also noticed by other seismologists, notably LEHMANN (1934), and appeared prominently with both P and S waves in the JEFFREYS-BULLEN revision (1935). Existence of the bend implies the onset of relatively rapid increases in the P and S velocities. The presence of such a bend complicates the calculation of the velocity distributions, and, in the course of his determination, JEFFREYS had much trouble in deciding whether finite discontinuities in the actual P and S velocities were indicated, or merely discontinuities in the velocity gradients. On balance, he found the latter hypothesis to be somewhat the more probable, and this finding has been followed in Table I. On the formal solution of JEFFREYS, the velocity gradients in the region C steadily diminish with increase of depth until a depth of 900 to 1000 km is reached, and are then fairly steady for the next 1700 km. Because of the smoothness of the changes near 1000 km, the depth selected for the base of the region C is somewhat arbitrary, but this arbitrariness is of no significance.

GUTENBERG (1951) has not found evidence of the 20° discontinuity, and his gradients run fairly steadily from a depth of 150 km to about 1000 km, where, however, there is a sharp reduction in the gradients. GUTENBERG's actual velocity values at 1000 km agree fairly closely with those shown in Table I.

LEHMANN's (1954) most recent examination of travel-time data leads her to suggest that it may be necessary to shift the location of a sharp change in gradients from 410 km to a less depth which might be as high as 200 km. But she concludes that the data at present available do not enable the depth to be at all precisely determined.

What does appear to emerge from the work of JEFFREYS, GUTENBERG and LEHMANN is that somewhere between depths of about 200 and 900 km the velocity gradients are greater than normal. A possible alternative is that there is a first-order discontinuity in the velocities at some depth between about 200 and 500 km. There is a possibility that future work of BENIOFF (1953) and of EWING and PRESS (1954) on very long surface waves may throw some light on this question.

Region D

The region *D* extends from 1000 km to a depth of nearly 2900 km where the *P* velocity changes abruptly from 13·6 to 8·1 km/sec and the *S* velocity drops effectively to zero. The regions *A*, *B*, *C* and *D* together constitute the Earth's mantle. The mantle is essentially solid throughout, since *S* as well as *P* waves are detected over the whole range of depth. The first good estimate of the depth of the base of the mantle was made by GUTENBERG (1914) in 1912. The latest estimate, made by JEFFREYS (1939d) and which relates to the standard sphere defined in Section 2, is 2898 ± 3 km.

Inside *D*, the velocity gradients are steady and moderate down to a depth of about 2700 km, but are not distinguishable from zero in the lowest 150 to 200 km of the mantle; the subdivisions *D′* and *D″* refer to these two parts of *D*. Earlier work of DAHM (1936) had suggested discontinuous velocity changes at a depth near 2700 km, but the work of both JEFFREYS and GUTENBERG implies that the changes are continuous.

It is important to note that, whereas the velocity distributions of JEFFREYS and GUTENBERG show some important differences in the regions *B* and *C*, their results agree very closely throughout *D′* and *D″*. A recent important work of BIRCH (1952) shows that the velocity gradients in *D′* are compatible with a uniform chemical composition in that region.

Region E

The existence of a "central core" was established by OLDHAM (1906) and this term has been applied to the whole region of the Earth below a depth of 2900 km. In the outer part, i.e. the region *E*, extending down to a depth of about 4980 km, the *P* velocity gradient is fairly steady and is comparable with that in *D′*. It is also probable that the chemical composition inside *E* is fairly uniform. The *P* velocity values of JEFFREYS and GUTENBERG are in fairly good agreement throughout most of the region *E*.

It is well established that the region *E* is in an essentially fluid state. Data on the tidal yielding of the solid outer part of the Earth, taken in conjunction with evidence on the variation of latitude, lead to an estimate of the Earth's overall rigidity. Values of the rigidity throughout the mantle are now fairly well known (see Section 6). It then becomes possible to estimate the rigidity of the core. The mathematical difficulties are considerable, but important steps towards solving the problem were taken by a large number of authors, including HERGLOTZ, LOVE, SCHWEYDAR, JEFFREYS, ROSENHEAD and STONELEY (JEFFREYS, 1952, Section 7.05). More recently, TAKEUCHI (1950) has shown that the central core, if assumed homogeneous, could not have a rigidity exceeding 10^{10} dyn/cm^2. This value may be compared with the rigidity near the base of the mantle which is about 3×10^{12} dyn/cm^2, and with the incompressibility in both the lower mantle

and outer core which is about 6×10^{12} dyn/cm^2. Since the region *E* occupies 94 per cent of the volume of the whole central core, it then follows that the region *E* must be in an essentially fluid state. This conclusion is confirmed by the total absence of reliable evidence of the occurrence of *S* waves in the region *E*.

The distribution of the *P* and *S* velocities in the Earth may thus be assumed to be fairly well known down to a depth of nearly 5000 km, the *S* velocity in the region *E* being taken to be effectively zero. There is no immediate inference possible about the *S* velocity below this depth, since the result of TAKEUCHI does not preclude the existence of significant rigidity below the region *E*.

Region F

In determining his 1939 velocity distribution, JEFFREYS (1939c) found that he could not fit the arrival-time data unless the *P* velocity decreased sharply over a range of depth just below the region *E*. His evidence, which rested in large part on readings of the deep-focus Solomon Islands earthquake of 1932 January 9, indicated that v/r varied at most, slightly, in the region *F*, the condition (12) being almost, if not actually, realized. In the absence of evidence to determine the detailed form of the *P* velocity variation in *F*, JEFFREYS formally assumed that the left-hand side of (12) is zero in *F*, and this led to the velocity value at the base of *F* shown in Table I; but the value is of course somewhat arbitrary.

A later study by JEFFREYS (1942) of the record deep-focus earthquake in the Celebes Sea of 1934 June 29 has supported the existence of the region *F*.

It needs to be remarked that GUTENBERG's velocity distribution does not show the region *F* at all, although GUTENBERG has informed the writer privately that, because of the narrow range of depth involved and of various uncertainties, his data do not preclude the existence of the layer *F*.

Region G

Between a depth of about 5120 km and the centre of the earth is the "inner core", the region *G*. Its existence was postulated by LEHMANN (1936) in order to explain various *P* readings on seismograms at distances short of 142°; in the absence of an inner core in which the *P* velocity is sharply greater than in the region *E*, there would, apart from diffraction effects around the outer core boundary, be a shadow zone caused by the drop in the *P* velocity between D'' and *E*. GUTENBERG and RICHTER (1938) supported Miss LEHMANN's hypothesis. The existence of an inner core became widely accepted when, in 1939, JEFFREYS (1939a, pp. 548–561) showed that the alternative suggested explanation—that the readings in question were due to diffraction—was untenable.

On the formal JEFFREYS solution, the *P* velocity jumps discontinuously from *F* to *G* by 18 per cent, from 9·5 to 11·2 km/sec, and thereafter increases very slowly to 11·3 km/sec at the Earth's centre. JEFFREYS (1952, Section 3·16) states that the velocities in the inner core are likely to be accurate within 0·5 per cent.

In GUTENBERG's solution, there is no discontinuous change in the *P* velocity anywhere in the central core, but there is a sharp change of gradient near the boundary of *G*, the velocity increasing from 10·1 to 11·2 km/sec between depths of about 5100 and 5350 km. From the latter depth to the centre, GUTENBERG finds the *P* velocity to be nearly constant, and his values do not differ from those of JEFFREYS by more than 0·1 km/sec.

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It needs to be remarked that the depths of the boundaries of F and G are uncertain by 50 km or more. Three significant figures are included in the depths shown in Table I only to prevent the introduction of rounding-off errors from the results of JEFFREYS which were presented in the form of fractions of the core radius.

5. THE PROBLEM OF THE EARTH'S DENSITY VARIATION

There are two well-established pieces of numerical data which the density variation in the Earth must fit. The first is that the mean density of the Earth is 5·517 g/cm^3, the corresponding value of the mass M being $5{\cdot}977 \times 10^{27}$ g; these values are correct within about one part in 1300 (JEFFREYS, 1952, Section 4·024). The second is that the moment of inertia I of the Earth is $0{\cdot}334Ma^2$, where a is the mean radius, the third figure in the decimal being slightly uncertain (JEFFREYS, 1952, Section 4·04).

An early model form of the Earth's density variation was given by the Laplace law, which corresponds to a chemically homogeneous Earth for which $dk/dp = 2$ throughout, k and p being the incompressibility and pressure, respectively. It can be deduced that this equation of state yields the formula

$$\rho = Ar^{-1} \sin Br$$

for the density variation, where A and B are constants. The values of A and B can be determined on using the data for M and I, and the result gives 2·8 and 11·2 g/cm^3 for the densities at the outside surface and the centre, respectively.

ROCHE's hypothesis was

$$\rho = A - Br^2,$$

and yielded 2·3 and 10·1 g/cm^3 for the outside and central densities.

WIECHERT allowed for a core in the Earth, but, in order to get a determinate result, treated the mantle and core as having constant densities ρ_0 and ρ_1, say. His results, which were based on an early and too-large value of the core-radius were ρ_0, $\rho_1 = 3{\cdot}2$, 8·1 g/cm^3. An amendment by JEFFREYS (1929), using later and better data, gave ρ_0, $\rho_1 = 4{\cdot}27$, 12·04 g/cm^3.

The need for a more detailed knowledge of the Earth's density variation arose in the course of computing the ellipticity corrections to the travel-time curves, the corrections depending on the ellipticities of internal surfaces of equal density as well as on the ellipticity of the outside surface.

From (4) and (5), we have

$$\frac{k}{\rho} = \alpha^2 - \frac{4}{3}\beta^2 = \phi, \text{ say}; \quad \frac{\mu}{\rho} = \beta^2. \qquad \ldots.(13)$$

We have seen from Section 4 that ϕ and β^2 are fairly well determined down to a depth of nearly 5000 km, so that k/ρ and μ/ρ are likewise fairly well determined. If values of a third function of k, μ and ρ, independent of ϕ and β^2, were known in the Earth, it would be a matter of simple algebra to deduce the variations of all three of k, μ and ρ down to 5000 km. No such values are directly available, but it has proved possible to make substantial progress by an indirect procedure which involves the variation $d\rho/dz$ of the density with the depth z below the outer surface.

Among other things, the density will depend on the pressure p. The pressure

is here considered to be the mean of the three principal stresses, with minus sign attached because of the conventional sign difference between the stress of elasticity and the pressure of hydrostatics. Thus

$$p = -\tfrac{1}{3}\Sigma p_{kk}. \qquad \ldots.(14)$$

The density will also depend on the temperature T. It will be sufficient, and more convenient, to take the entropy S as argument, rather than T. Also the density will depend on an indefinite number of parameters, n_i say, specifying the chemical composition. Thus, strictly, one should write

$$\rho = \rho(p, S, n_i).$$

If we limit consideration to a chemically homogeneous region, however, we can write

$$\frac{d\rho}{dz} = \left(\frac{\partial\rho}{\partial p}\right)_S \frac{dp}{dz} + \left(\frac{\partial\rho}{\partial S}\right)_p \frac{dS}{dz}. \qquad \ldots.(15)$$

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Let α_p be the coefficient of thermal expansion at constant pressure, and τ the excess of the actual temperature gradient over the adiabatic temperature gradient, at the depth z. Then

$$\alpha_p = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_p,$$

and

$$\begin{aligned}\tau &= \frac{dT}{dz} - \left(\frac{\partial T}{\partial p}\right)_S \frac{dp}{dz} \\ &= \left(\frac{\partial T}{\partial S}\right)_p \frac{dS}{dz} \\ &= -\frac{1}{\rho\alpha_p}\left(\frac{\partial\rho}{\partial S}\right)_p \frac{dS}{dz}.\end{aligned}$$

Thus (15) becomes

$$\frac{d\rho}{dz} = \left(\frac{\partial\rho}{\partial p}\right)_S \frac{dp}{dz} - \alpha_p\rho\tau. \qquad \ldots.(16)$$

By (2) and (14), again assuming chemical homogeneity, we have

$$dp = -kd\theta = k\frac{d\rho}{\rho}, \qquad \ldots.(17)$$

i.e.

$$\left(\frac{\partial\rho}{\partial p}\right)_S = \frac{\rho}{k},$$

where k is the adiabatic incompressibility. Also, by the theory of gravitational attraction,

$$\frac{dp}{dz} = g\rho, \qquad \ldots.(18)$$

where g is the value of gravity at the depth z. Hence (16) becomes

$$\frac{d\rho}{dz} = \frac{g\rho^2}{k} - \alpha_p\rho\tau. \qquad \ldots.(19)$$

The form (19), neglecting the term in τ, was used by WILLIAMSON and ADAMS (1923) in examining the density variation in the outer mantle, and by BULLEN (1936) in an attack on the density variation in the whole Earth. The form of the

term in τ is due to BIRCH (1952), though derived by him in a different way from the above.

BIRCH has examined the term in τ in some detail using his own and others' experimental data, and concludes that a departure of 1 deg/km from the adiabatic temperature gradient may affect the estimated value of $d\rho/dz$ by the order of 10 per cent. In the deep interior, below the region C, the work of VERHOOGEN (1954) and UFFEN (1952) on temperature variation makes it likely that the effect would be appreciably less than 10 per cent at most depths. It is then probable that the ignoring of the term in τ does not lead to errors in the computed densities exceeding about 0·1 g/cm^3. It may be remarked further that the effect on $d\rho/dz$ of allowing for small progressive changes of composition in a region to which (19) is applied would be in the opposite direction to the effect of allowing for τ.

Neglecting τ, (19) can by (13) be written as

$$\frac{d\rho}{dz} = \frac{Gm\rho}{r^2\phi}, \qquad \ldots.(20)$$

where G is the constant of gravitation, and m is the mass contained within a sphere of radius r. The equation (20) can be applied to any assumed chemically homogeneous layer, provided starting values of m and ρ are available, along with the relation

$$\frac{dm}{dr} = 4\pi r^2\rho. \qquad \ldots.(21)$$

An adequately accurate starting value of m for the top of the layer B is derived, knowing the mass M of the Earth and subtracting off a conventional allowance for the crust. A starting value, ρ' say, of ρ cannot be obtained without appeal to further evidence. Three lines of evidence have been brought to bear on this point, namely: (i) the general increase of basicity, with depth, of rocks in the outer part of the Earth, and the broad correlation between basicity, density and seismic velocities; (ii) geophysical laboratory experiments which imply that the densities of rocks for which k/ρ and μ/ρ come close to fitting the seismic data for the top of the region B are close to the range 3·3–3·4 g/cm^3; (iii) the fact that the mean density of the Moon is 3·34 g/cm^3 and that there are reasons for believing that ρ' should not exceed this density.

In 1936, (20) and (21) were applied (BULLEN, 1936) throughout the whole of the regions B, C and D, the value of ρ' being taken as 3·32 g/cm^3 which would agree with an olivine composition. (Even if the composition is not olivine, subsequent work has given no ground for changing the figure of 3·32.) In this way, formal distributions of ρ and m were derived throughout the mantle. Using the known moment of inertia of the Earth and the relation

$$\frac{dI}{dr} = \frac{8}{3}\pi r^4\rho,$$

it was then found that the yielded moment of inertia of the core was 0·57 $(mr^2)_1$, where the subscript 1 applies to the core boundary. Such a result is of course impossible on stability considerations, since the coefficient 0·57 exceeds the value 0·40 which applies to a sphere of constant density.

This impossible result implied that at least one of the assumptions made is

faulty. The assumptions to be considered are: (a) neglect of the term in τ; (b) use of the value 3·32 g/cm³ for ρ'; (c) neglect of deviations from chemical homogeneity. Examination has shown that allowance for τ would increase, not decrease, the impossible coefficient 0·57. Next, in order to bring the coefficient down to below 0·40, ρ' would have to be at least 3·7 g/cm³, a value which is higher than geologists and geophysicists are prepared to accept. Hence it follows, with extremely high probability, that the faulty assumption is (c), so that there must be marked chemical inhomogeneity (or possibly a polymorphic transition) in the mantle somewhere between the crust and the core. Further numerical analysis shows that the inhomogeneity must occur a long way above the core and, most probably, in the region above a depth of 1000 km.

Although this result was established nearly twenty years ago, it has lately become prominent because of the recent interest in cyclic convection current theories in the mantle. BIRCH (1954) has pointed out that the result in question is a serious obstacle to these theories, although the obstacle is not quite insuperable (BULLEN, 1954a).

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It thus becomes necessary to abandon the use of (20) throughout a part of the mantle. Over the period 1940–42 (BULLEN, 1940; 1942), the effect of using (20) in the regions *B* and *D* and the core, but not in *C*, was examined. Indeterminacy in the solution arose through uncertainty of the density in *C* and consequently in the starting value for ρ at the top of *D*, and also through ignorance of the density at the Earth's centre. The facts that m has to be zero at $r = 0$, and that the density distribution has to fit the Earth's moment of inertia, however, provided powerful controls on the allowable distribution, except inside the inner core. Also, since, by (4) and (5), α and β are functions of ρ, it follows that discontinuities in ρ or its gradient must, almost certainly, be accompanied by similar types of discontinuity in the velocity variations. Hence, if the velocity distributions summarized in Table I be accepted, the density will change continuously between *B*, *C* and *D*, and the density gradient will be discontinuous at the top of *C* but continuous between *C* and *D*.

On these considerations, it emerged that the density ρ'' at the Earth's centre must be at least 12·2 g/cm³, but no upper bound to the central density was indicated. It was found that increasing ρ'' by 5 units above the indicated minimum would increase the formally computed densities in the mantle by amounts never greater than 0·03 g/cm³, and reduce the values in the region *E* by only 0·4 g/cm³. In this way it became possible, on the assumptions made, to derive a good determination of the Earth's density variation down to a depth of nearly 5000 km.

6. THE EARTH MODEL *A*

The name Model *A* has been given (see BULLEN, 1953a) to an Earth model constructed according to the pattern just outlined, the density at the centre being arbitrarily taken as 17·3 g/cm³. In the light of developments since 1942, there is a possibility that some small correction may be needed because of uncertainties in the seismic data in the regions *B* and *C* and of possible deviations from the form (20) in the region *B*. The compressibility hypothesis, to be discussed in Section 7, also suggests some small changes near the core boundary, as will be seen.

The distribution of k and μ in Model *A* (down to the base of the region *E*)

is immediately computed from the density distribution and the seismic data, using (13). The distribution of g is deduced using $g = Gm/r^2$, and that of p is then derived using (18). The values of ρ, p, k and μ at certain of the depths involved in Table I are shown in Table II. No values of k and μ are included below the region E both because the central density of 17·3 g/cm³ has been arbitrarily taken, and because of ignorance (at this stage) of the rigidity in the inner core.

Table II. Properties of Earth Model A

Depth (km)	Density (g/cm^3)	Pressure (10^{12} dyn/cm²)	Incompressibility (10^{12} dyn/cm²)	Rigidity (10^{12} dyn/cm²)
33	3·32	0·01	1·16	0·63
410	3·64	0·14	1·73	0·90
1000	4·68	0·39	3·60	1·90
2900	5·69 9·4	1·37	6·5 6·2	3·0 <0·01
4980	11·5	3·17	12·6	<0·01
6370	17·3	3·64		

The results for g are interesting in that g keeps within 1 per cent of 990 cm/sec² down to a depth of 2400 km. This near-constancy of g throughout the greater part of the mantle is well-established as it is a feature of other models some of which are rather different from Model A. The maximum of g, equal to about 1040 g/cm³, occurs at the core boundary, and inside the core g diminishes continually to zero at the centre.

In Model A, Young's modulus ranges from $1{\cdot}60 \times 10^{12}$ dyn/cm² at the top of the region B to $7{\cdot}87 \times 10^{12}$ dyn/cm² at the base of the mantle; Poisson's ratio σ from 0.269 to 0·300; and the Lamé elastic constant λ (equal to $k - 2\mu/3$) from $0{\cdot}74 \times 10^{12}$ dyn/cm² to $4{\cdot}49 \times 10^{12}$ dyn/cm². In the fluid region E, σ is of course equal to 0·5 and Young's modulus to zero, while λ is equal to k.

7. COMPRESSIBILITY AND PRESSURE

A striking feature of Model A is that, whereas the density ρ and rigidity μ suffer major changes at the core boundary at depth 2900 km, there is little change indicated in the incompressibility k. The formally indicated change, a reduction of 5 per cent, is, moreover, not necessarily real because of uncertainties in the postulates underlying Model A.

A second striking feature comes to light on examining values of dk/dp in the regions extending a few hundred kilometres on either side of the core boundary. By (13) and (17), we have, in a region where chemical inhomogeneity and departures from an adiabatic temperature gradient can be neglected,

$$\frac{dp}{d\rho} = \phi;$$

and hence

$$\frac{dk}{dp} = \frac{d(\phi\rho)}{\phi d\rho}$$
$$= 1 + \frac{\rho d\phi}{\phi d\rho}$$
$$= 1 + g^{-1}\frac{d\phi}{dz}, \qquad \ldots.(22)$$

since $d\rho/dz = g\rho/\phi$.

In the lowest 200 km of D', i.e. between depths of 2500 and 2700 km, $d\phi/dz$ as determined directly from the seismic data is $2{\cdot}2 \times 10^3$ c.g.s. units, whereas $d\phi/dz$ sinks to zero in D''. Since g is close to 1000 cm/sec^2 in both D' and D'', (22) would imply that dk/dp sinks from 3 units to 1 unit in D''. This implies that D'' is physically different from D', and hence, the velocity changes being continuous, that D'' is a region of varying composition (or possibly a region where polymorphic transitions occur). Hence (22) is inapplicable to D'', and fails to yield a reliable value of dk/dp in D''.

The value of $d\phi/dz$ in the outermost 200 km of the region E is, however, equal to that near the bottom of D', within the uncertainty of the determination. Since it is highly probable that D' and E are close to chemical homogeneity, and since the differences in g are small, it follows that dk/dp is practically the same at the bottom of D' and at the top of E, the indicated values being close to 3 units.

The near-continuity of both k and dk/dp between D' and E in Model A, taken in conjunction with experimental data which showed that increasing pressure tends to diminish differences in compressibility between different materials, led to the setting up of a hypothesis (BULLEN, 1946) that at pressures of the order of a million atmospheres the compressibility of a material is determined by the pressure rather than by the chemical composition. More recent work in theoretical physics (FEYNMAN *et al.*, 1949) indicates that the hypothesis in this form is a little too wide in that there is some small variation of k with atomic number at high pressures. The range of variation of the representative atomic number inside the Earth below a depth of 1000 km is, however, likely to be sufficiently small for the hypothesis to be a valuable approximation in this region.

This compressibility hypothesis has led (BULLEN, 1949a) to interesting suggestions on the physical properties of the regions D'', F and G.

It has already been seen that the equation (20) fails to find the nature of the variation of density in D''. But this variation can be determined from the compressibility hypothesis by thus setting dk/dp equal to about 3 units, the value prevailing immediately above and below D''. Since, according to the seismic data, ϕ is nearly constant in D'', the relation $k = \rho\phi$ then gives $dk/d\rho \approx \phi$. Hence, in D'',

$$\frac{d\rho}{dz} = \frac{d\rho}{dk}\frac{dk}{dp}\frac{dp}{dz}$$
$$\approx \frac{1}{\phi} \times 3 \times g\rho,$$

the last expression being three times the value $g\rho/\phi$ which (20) would formally yield. The compressibility hypothesis therefore implies the presence of an accumulation of denser matter in the lowest 200 km of the mantle, the density

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gradient there being about three times the normal. Recent experimental and theoretical evidence confirm that dk/dp must be nearer 3 units than 1 unit at the pressure involved, and the conclusion just drawn can be shaken only if the seismic data for D'' prove to be faulty.

By an argument fairly similar to that just used, the compressibility hypothesis implies that the density gradient in the inner core G is also significantly greater than normal, the P velocity gradient being again much less than normal. Again a progressive change of composition in G is indicated, and the total change of density inside the inner core is formally given as about 3 g/cm^3.

Assuming the region F to exist, the same type of argument leads to an abnormally high density gradient in F, the gradient being much steeper in this case because of the negative velocity gradient. On the Jeffreys model, the density changes in F would amount to 3 g/cm^3, though this figure must be regarded as rather uncertain because of the arbitrary form of velocity variation assumed by JEFFREYS in F.

The next interesting inference is that the compressibility hypothesis implies that the inner core is solid. This inference comes from the seismic evidence on the increases in the P velocity from the outer to the inner core. On the Jeffreys data, α jumps by 18 per cent between F and G, and therefore α^2 by nearly 40 per cent. If the inner core were fluid, the relations (6) would apply; and, since it is virtually impossible that ρ should decrease at this depth with increasing depth, k would have to suffer a discontinuous change of about 40 per cent or more, in contradiction to the compressibility hypothesis. The contradiction can, however, be simply resolved by replacing (6) by (4), namely

$$k + \tfrac{4}{3}\mu = \rho\alpha^2,$$

and assuming that in the inner core there is rigidity given by

$$\tfrac{4}{3}\mu = 0{\cdot}40k.$$

On the Gutenberg seismic data, a similar conclusion is indicated except that the implied value of μ is only about half as great. The data of JEFFREYS and GUTENBERG are opposite extremes in that the former involves a decrease of velocity (in F) followed by a discontinuous increase, while the latter shows no velocity decrease and only a gradual increase. It is therefore to be expected (BULLEN, 1953b) that the inner core value of μ lies between 2 and 4×10^{12} dyn/cm^2, which are approximately the values derived from the two sets of data. The smaller of the values corresponds to a rigidity about $2\frac{1}{2}$ times that of steel at zero pressure.

Support for the solidity of the inner core comes from a consideration of data on Thomas-Fermi-Dirac matter at pressures above 10^7 atm (FEYNMAN *et al.*, 1949), geophysical data, and high-pressure experimental data. Adaptation (BULLEN, 1952a) of an extrapolation made by ELSASSER (1951) shows that any jump in k between the regions E and G is likely to be less than 5 per cent and may be zero, and such a jump is less than a quarter of the minimum required if the inner core is to be fluid.

Various writers, for example JACOBS (1953, 1954) and SIMON (1953), have provided plausible physical grounds for the existence of an inner core with a rigidity as above indicated, and BIRCH (1940) has previously suggested a connection with the alpha-gamma transformation of iron. CHANDRASEKHAR finds that a sharp boundary such as a solid inner core would provide would make it easier

for the mode of convection currents, envisaged by ELSASSER (1950) and BULLARD (1950) in their theory of the Earth's magnetic field, to occur in the fluid outer core.

8. THE EARTH MODEL *B*

In 1950, a second Earth model (BULLEN, 1950b), called Model *B*, was set up in which it was explicitly postulated that k varies smoothly between a depth of 1000 km and the Earth's centre. It was found that this postulate, taken in conjunction with the use of (20) only in the regions D' and E (where, as has been seen, the evidence for chemical homogeneity is relatively strong), and with the use of the values of the Earth's mass, radius and moment of inertia, was sufficient to give the density distribution from the centre to within 200 km of the outer surface, independently of any starting value of the density. Seismic data were used in D'', F and G, but only in conjunction with the compressibility hypothesis and not with (20).

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In the regions *B* and *C*, no reference at all was made to the seismic velocity data. It transpired that the postulates of the last paragraph required the density gradient found in D' to be continued upward steadily to a depth not greater than 200 km below the outside surface. In Model *B* it was not possible to make the density follow a similar form to the velocity curves between depths of 200 and 1000 km, as was done in constructing Model *A*. Should Model *B* prove to be nearer the truth than Model *A*, it would be likely (BULLEN, 1954a) that the changes in the Earth associated with the 20° discontinuity should be nearer 200 than 400 km depth, as has been suggested independently by Miss LEHMANN.

This last feature of Model *B* is a consequence of removing the small discontinuous change in k that was formally indicated in Model *A* at the core boundary. Small though the change is, its removal demands increases in density in the region *C* and in the lower part of *B*. It may be remarked that there are really two aspects of the compressibility hypothesis, namely (i) continuity in k; (ii) continuity in dk/dp. The independent evidence favouring strict adhesion to (i) is not quite as strong as that favouring (ii), so that no firm conclusion can be drawn from the above argument about the location of the 20° discontinuity. There is, however, a further point in that the indicated change in k in Model *A* is a *reduction* from the mantle to the core, whereas physical theory suggests that any change is more likely to be an increase than a reduction. This argument would favour Model *B*, were it not for some uncertainties in extrapolations from the physical theory used. (Most other properties of Model *B* do not depend on the strict application of (i) and, in the light of the evidence from theoretical physics, are somewhat more firmly based.)

An important property of Model *B* is that it gives the first indication of the density in the inner core. The formal calculations lead to a value at the Earth's centre of 17·9 g/cm^3 (neglecting possible small accumulations of denser matter on a scale below what seismic evidence could reveal). The value is rather uncertain because of the uncertainties in the seismic *P* velocity variation in *F*, but (BULLEN, 1955) cannot be less than 14·5 g/cm^3 compatibly with the compressibility hypothesis.

Of possible interest in physics is the relation between k and p which emerges for Model *B*. Between depths of 1000 and 5000 km, the relation

$$k = 2{\cdot}25 + 2{\cdot}86p + 0{\cdot}16p^2, \qquad \ldots.(22)$$

where the units of k and p are 10^{12} dyn/cm^2, fits Model B within 2 per cent. The value of dk/dp given by (22), namely $2{\cdot}86 + 0{\cdot}32p$, is markedly greater than the value involved in the Laplace law. The equation (22) gives an equation of state, relevant to a pressure range from 0·4 to $3{\cdot}2 \times 10^{12}$ dyn/cm^2, which it will be interesting to check against future physical evidence for materials whose atomic numbers are of the order of those in the regions D and E of the Earth, i.e., presumably, between 12 and 28.

Values of ρ, p, k and μ at certain depths in Model B are shown in Table III. It will be noticed that the deviations from the values in Model A are mostly small. Values of the density and pressure are not given at depths less than 200 km since there is no evidence to show that they are different from the Model A values. Values of k and μ are not shown at depths above 1000 km, since the density distribution in Model B favours some revision of the seismic velocity values, on which the derivation of values of k and μ would depend, above this level.

Table III. Properties of Earth Model B

Depth (km)	Density (g/cm^3)	Pressure (10^{12} dyn/cm^2)	Incompressibility (10^{12} dyn/cm^2)	Rigidity (10^{12} dyn/cm)^2
200	3·94	0·07		
410	4·07	0·15		
1000	4·41	0·40	3·4	1·8
2900	5·57 9·7	1·33	6·4	3·0 <0·01
4980	12·0	3·22	13·1	<0·01
5120	15·0	3·33	13·6	<0·01 3·6
6370	17·9	3·94	17·4	4·0

A further examination of the postulates involved in Models A and B makes it highly probable (BULLEN, 1955) that, in the regions D and E, the density values in the actual Earth lie between the Model A and Model B values, and the same applies to the compressibility values. It will be noticed that the pressures in the two models are in fairly close agreement down to a depth of 4980 km. It is highly probable that the pressure at the centre of the Earth lies between 3·6 and 4 million atmospheres.

The values of the rigidity shown for the inner core in Model B are based on the formal Jeffreys velocities. As has been seen, these rigidity values could be rather less. Rigidity in the inner core implies that S waves could be transmitted throughout, and theoretical travel-times, based on Model B and the J.-B. tables, have been prepared (BULLEN, 1950c, 1951a) for a phase *PKJKP*, where P corresponds to segments of a ray in P type in the mantle, K to segments of P type in the outer core, and J to a segment of S type in the inner core. The energy in

such a phase has, however, been found at the most favourable epicentral distance to be only, at most, 0·04 of that in the companion phase *PKIKP*, where *I* corresponds to a segment of *P* type in the inner core. (On the Gutenberg velocity distribution, the energy factor would be appreciably less than 0·04.) This means in practice (BURKE-GAFFNEY, 1953) that the phase *PKJKP* is only at best on the border of observability, and that there will be much difficulty in determining the inner core rigidity in this way. (On the other hand, had the energy factor turned out to have been much greater than 0·04, the fact that a phase that would correspond to *PKJKP* has not to date been observed in routine readings of seismograms would have argued against the existence of rigidity in the inner core.)

9. RELATED QUESTIONS OF COMPOSITION

The contribution of seismology to knowledge of the structure of the Earth's deep interior is best summarized in terms of the numerical results discussed in the preceding sections. The results, however, impinge on questions of composition, and, although these questions are mostly highly controversial, a few remarks about them may not be out of place in the present chapter. It needs to be stressed that, in the present state of knowledge of the composition of the deeper interior, the various sources of evidence are best treated with a cautious empiricism.

In regard to the composition of the mantle, it has been stated by ADAMS and WILLIAMSON a few years ago that there are no measurements which conflict seriously with the conclusion that the mantle consists of ultrabasic rock. Dunite, a fairly pure form of olivine, $(Mg, Fe)_2 SiO_4$, has been favoured as the rock in the region *B* by a large number of authors, and this has lately been supported in the work of HESS (1954). Among other rocks which have been considered are peridotite and eclogite (see also BIRCH, 1952).

To account for the changes in the region *C*, JEFFREYS and BERNAL (1936) suggested a transition from orthorhombic to cubic olivine brought about by the high pressure. BERNAL pointed out that magnesium germanate, which is chemically analogous to forsterite (Mg_2SiO_4), undergoes such a change of crystal structure at moderate pressures. A calculation indicates that the associated density change in the case of olivine, would be about 9 per cent, a little short of the overall density changes in the region *C* of Model *A*, but of the right order. BRIDGMAN (1951) has incidentally found a discontinuous change in the shearing strength of olivine at a pressure of $0{\cdot}084 \times 10^{12}$ dyn/cm^2, which corresponds to a depth of 250 km below the Earth's outer surface. On the JEFFREYS-BERNAL hypothesis, the composition would be predominantly cubic olivine in the region *D*.

BIRCH (1952) considers that the region *C* may be associated with a change of proportion of MgO, FeO and SiO_2, regarded as distinct phases. He suggests that the region *D* may consist "of high pressure phases, possibly closely-packed oxides of magnesium, silicon and iron, similar in structure to corundum, or rutile or spinel", but that further studies by the methods of chemical physics are needed.

No generally accepted explanation is available of the relatively high density gradient indicated in the region *D″*. One suggestion has been that sulphides are present, but BERNAL has pointed out that the relative sizes of sulphur and

oxygen ions are likely to prevent mixed sulphide-silicate crystals from forming readily.

For a long time it has been assumed that the central core is composed of iron or nickel-iron. This view was developed by WIECHERT near the beginning of the century in order to explain the relatively high density in the core. Also the idea derived some support from early observations of meteorite compositions.

In 1941, KUHN and RITTMANN (1941) put forward a view to the effect that the central core is largely composed of compressed hydrogen. There are various cogent arguments against this theory, especially the difficulty of explaining why the densities of the outer planets are so low. But the work of KUHN and RITTMANN has stimulated interest in theories that the central core is not largely composed of iron.

In 1937, JEFFREYS (1937) had shown that if the planets Mars, Venus and the Earth, are (in the large) each composed of a rocky mantle and central core, the material of the central core being chemically distinct from that in the mantle, and the density variation in each part being essentially determined by pressure, then the overall compositions of these planets must be different (see also BULLEN, 1937a). The calculation showed that, to fit the observed diameters and masses, the proportions by mass of mantle to core would have to be 4 : 1 in the case of Venus and 5 : 1 in the case of Mars, as against 2 : 1 in the case of the Earth. There was no possibility of explaining the discrepancies in these ratios by uncertainties in the observational data or by errors in the figures used for the Earth's density variation.

KRONIG, DE BOER and KORRINGA (1946), in seeking to examine the KUHN-RITTMANN Theory, calculated theoretically that, at 700,000 atm, hydrogen would change to a metallic state which would have the property of high electric conductivity; the atoms would become so closely spaced that electrons, instead of remaining each associated with one particular atom, would become free to roam through the whole structure. Moreover, at the pressure stated, the density of hydrogen would suddenly change from 0·4 to 0·8 g/cm^3.

RAMSEY (1948) associated this result with examinations he had been making of phase transitions at high pressures, and suggested that the density increase from about 5·7 to 9·4 g/cm^3 at the boundary of the Earth's central core is brought about by pressure and not by a change of chemical composition, the central core being composed not of iron or nickel-iron, but of a metallic form of ultrabasic rock, the circumstances being somewhat analogous to (but naturally more complicated than) the case of hydrogen. RAMSEY found further that this notion brought in its train the possibility of the planets Mars, Venus and the Earth having a common primitive composition. On the new theory, the density would be determined essentially by pressure throughout the whole of each planet, instead of there needing to be separate pressure-density relations in the mantle and central core as had been assumed by JEFFREYS. RAMSEY used the Earth Model *A* in his calculations, and found that the new assumption largely removed the discrepancy in overall composition that had been found by JEFFREYS in the case of Venus and the Earth. There was, however, still an appreciable discrepancy in the case of Mars, though rather less than on the JEFFREYS assumption. RAMSEY sought to remove the discrepancy by an ad hoc modification to Model *A* in the form of a small increase to the density gradients at all depths;

this would correspond to a slow steady change of composition throughout the Earth, not more marked at the outer core boundary than elsewhere.

The result of KRONIG and others on hydrogen had also led the writer (BULLEN, 1949b–50a) to consider, in relation to planetary compositions, the possibility that the density change at the outer core boundary is brought about by pressure. The use of Model *A* led to the same measure of agreement as was found by RAMSEY. But it was seen that Model *B*, which was at the time being constructed (on a completely independent hypothesis), was going to deviate from Model *A* in just the right direction to remove the discrepancy with Mars without damaging the agreement with Venus. When, in fact, the calculations were completed, it was found that the following set of postulates fitted, within the standard errors, the observations of the masses and diameters of Mars and Venus that were available to the writer at the time:

(i) The Earth, Venus and Mars have a common primitive composition.

(ii) The density distribution of the Earth conforms to Model *B*.

(iii) The outer core of the Earth is a high-pressure modification of the material in the lower mantle.

(iv) The inner core is chemically distinct from the outer core and mantle. (Without the postulate (iv), the agreement is somewhat outside the standard errors.)

It was also found that the set of postulates (i) to (iv) leads to a value of 1/188 for the ellipticity of figure of Mars, as against 1/181 if the Earth's inner core is taken to have the same composition as the mantle and outer core. (The calculation is somewhat uncertain because it assumes that departures from hydrostatic conditions inside Mars are not serious.) The observed ellipticity (WOOLARD, 1944) is 1/192, $\pm \frac{1}{2}$ per cent. Thus there is some additional suggestion that the inner core is chemically distinct from the outer core.

The apparent extremely close agreement of (i) to (iv) with the relevant astronomical observations has since been a little disturbed because of revisions in the astronomical data that had been used. The radius of Mars calculated taking the mass as $6{\cdot}442 \times 10^{26}$ g, and using (i) to (iv), is 3390 km; if the postulate (iv) is dropped, the result is 3410 km; and if Model *A* is used in place of Model *B*, the result is 3520 km. An observational value that has been widely used is 3396 ± 8 km. UREY (1952) has drawn attention to the possible effects of a Martian atmosphere on the observations, and has suggested that TRUMPLER's value of 0·520 times the Earth's radius, or 3310 km, is a better value, being derived from observations of movements of surface markings. Dr. G. P. KUIPER in a personal discussion, has informed me that the preferred figure is now a little greater than 3330 km. Dr. KUIPER informs me that a reduction in the observational diameter of Venus is also indicated.

In these circumstances, it would appear that some little revision is called for in the postulates (i) to (iv). The revisions in the planetary data are in the direction of suggesting that, while (iii) may be still significant and important, the Earth's outer core contains some material of higher atomic number than that for the region *D*, in addition to high-pressure phases. If the discrepancy between the calculated value of 1/188 for the ellipticity of Mars and the observed value of 1/192 is not due to the hydrostatic assumption, the sign of this discrepancy also leads to a similar suggestion.

On this line of approach, the most probable conclusion is that the outer core

contains some uncombined iron and also material of lower representative atomic number in the form of a phase transformation of the material of the lower mantle.

In connection with this conclusion, it may be remarked that BIRCH (1952) has inferred that the density in the outer core "is perhaps 10 to 20 per cent lower than the density of iron or nickel-iron under similar conditions"; (BIRCH would ascribe the reduced density to the effects of alloying). Also KNOPOFF and UFFEN (1954) have used a quantum-statistical method to show that, if there is no phase transformation at the core boundary, the most probable atomic number representative of the region E is 22, four units less than that of iron, six units less than that of nickel. If there is a phase transformation at the core boundary, this atomic number would be lowered.

On the question of the composition of the inner core, the density distribution makes it practically certain that the representative atomic number is not less than 26. It is probable that iron and nickel predominate in the inner core, and the steeper-than-average density gradient suggests that some still denser materials may also be present. It does not seem profitable to speculate on the composition of the region F until the seismic velocity distribution in F is more precisely known.

A few closing remarks need to be made. The first is that whereas it is possible, without straining of the data, to fit the Earth, Venus and Mars into a common primitive overall composition—and there is little difficulty in bringing the Moon into the same picture—nevertheless Mercury is an apparent exception. If Mercury proved to be a real exception, then the use of planetary data would lose its force in the present context. The exceptional feature of Mercury is its high mean density, of order 5 g/cm^3 (RABE, 1950), which, because of the small size of Mercury, implies that the present Mercury cannot have the same composition as the Earth, Mars and Venus. But Mercury is also exceptional in that it is the closest planet to the Sun, and even at the present temperature at the subsolar point at perihelion, molecules of molecular weight up to about 70 would escape if volatilized. Since the orbit of Mercury is likely to have been more eccentric formerly, it is probable (BULLEN, 1952) that the surface temperature was earlier great enough to permit the volatilization of an appreciable part of the rocky mantle. Thus the primitive Mercury is likely to have been very differently composed from the present Mercury, so that current data are not relevant to the present discussion, except on one point. The point of interest is that the mean density of Mercury appears to have *increased* with loss of material to its present value of 5 g/cm^3, whereas a decrease would be implied if the density variation were entirely determined by pressure. The observations of Mercury therefore appear to serve almost as a crucial test of the presence, in terrestrial planets, of a quantity of material chemically distinct from that in the Earth's mantle, the proportion being at least equal to the proportion of the mass of the Earth's *inner* core to the mass of the Earth.

At the hands of RAMSEY and LIGHTHILL (1950), it has been shown that phase transformations of the type contemplated in the Earth's deep interior can be a source of gravitational instability in planets. This may possibly have been relevant to the formation of the Asteroids, or even of the Moon (BULLEN, 1951b; DATTA, 1954).

It needs to be remarked that some physicists, notably ELSASSER, hold the

view that theoretical considerations forbid a phase transformation of the type envisaged at the base of the Earth's mantle, if the accompanying density change is in as high a ratio as 1·6. Others hold that work carried out to date does not yet permit a judgment to be made, and theoretical attacks on the problem are at present being made in several centres. A summary of some of the work on phase transformations has recently been published by RAMSEY (1954).

The possibility of estimating the density change $\Delta\rho$ at the outer core boundary by a fairly direct method has lately been explored in an interesting paper by BÅTH (1954). The change $\Delta\rho$ would be involved both in the energy partitioning of waves reflected at the boundary, and also in changes of phase. From an examination of theoretical and observational aspects of the latter effect in the case of *PcP* seismic waves, BÅTH considers that it is clearly established that $\Delta\rho$ is greater than zero. If, through a development of the method, it becomes possible to estimate the actual value of $\Delta\rho$ to good precision, a most important check on the homogeneity of the regions D' and E will have been derived.

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THE HYDRODYNAMICS OF THE EARTH'S CORE

By RAYMOND HIDE

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1. INTRODUCTION

NOWADAYS we have a fairly good working model of the earth's interior, which was not available until a few decades ago. Geophysical data, mainly from seismology, reveal the existence of two major regions within the earth, namely, a dense metallic liquid core of radius rather more than one half of that of the whole earth, surrounded by a solid mantle of lower density material, probably olivine, a ferromagnesium silicate. (The thin crust overlying the mantle will not concern us here.)

The rapid secular changes of the earth's magnetic field have been interpreted as implying the existence of relative motions within the core. When different parts of a continuous body of fluid flow relative to one another, it is said that the fluid is in hydrodynamical motion.

Of the many theories of the origin of the earth's magnetism that have been advanced, none has been entirely successful and only those which attribute the phenomenon to ordinary electric currents circulating within the earth bear close quantitative examination.

The age of the earth is about 4×10^9 years. A system of electric currents once generated within it and left to decay freely would virtually disappear in only about 10^5 years, due to electrical energy dissipation through Joule heating. Hence, a mechanism for generating these currents and maintaining them against electrical resistance must exist.

Several suggestions as to the physical nature of this mechanism have been proposed. Of them, the most promising invoke the action of hydrodynamical motions in the core as an essential feature of the mechanism. Hence, an adequate theory of the earth's magnetism requires, in the first instance, a theory of core

hydrodynamics. It is the purpose of this paper to review the contributions to core hydrodynamics that have been made.

It will be necessary to examine the physical state of the earth's interior and the earth's magnetic field. This is done in Section 2 and Section 3, before the subject of the core hydrodynamics is discussed in the final Section 4. However since the problem of core hydrodynamics involves great theoretical difficulties which have not yet been overcome, (indeed even simple hydrodynamical situations do not readily lend themselves to mathematical analysis,) a few general comments will be made before concluding this introduction.

Some General Comments on Hydrodynamics

Phenomena of fluid motion occur widely in nature, each presenting its own particular problem. Several such problems confront the geophysicist.

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It has been suggested that the mantle which, although solid from the seismic point of view, can suffer deformation when acted upon by slowly varying forces, is in hydrodynamical motion. This flow has been invoked by some authors (VENING-MEINESZ, 1937) to account for certain features of the earth's topography; the velocities of flow involved would be very small, only about 1 cm/year.

Meteorologists and oceanographers have long studied two very important hydrodynamical problems, namely, the general atmospheric circulation and ocean currents, respectively. Even at the present day, their efforts cannot be said to have met with anything approaching complete success.

Within the bounds of the solar system we find many other hydrodynamical phenomena which still pose difficult problems. A glance at the sun's surface introduces us to but a few; explanations of solar flares and sunspots are still awaited (KUIPER, 1954). And without a satisfactory understanding of the circulation within their atmospheres our knowledge of the planets will remain incomplete (KUIPER, 1951).

On extending our gaze still further into the depths of space, we find that the tenuous medium pervading the vast interstellar regions is in hydrodynamical motion,* and there is less palpable, but none-the-less compelling, evidence arising from theoretical studies of stellar interiors that certain regions within many stars sustain fluid flow.

Although astronomy has made great strides of late through the application of "modern" physics, especially the theory of spectra, the field of application of hydrodynamics to the cosmos is almost untouched. It is, however, of some significance that at present astrophysicists are devoting some of their efforts to the development of theoretical hydrodynamics so that the enormous variety of fluid flow phenomena confronting them may eventually be understood.

It is probably true to say that nearly all naturally occurring fluid flow is due ultimately to the action of gravity. Two examples spring immediately to mind. The circulation of the atmosphere is due mainly to the action of the earth's (nearly) uniform gravitational field on density inhomogeneities caused by solar heating. The oceanic tides are due to the action of a variable gravitational field, produced by the rotation of the earth in the proximity of the moon, on a fluid of (nearly) uniform density. If gravity is the only driving force available, how then

* Symposium: Problems in Cosmical Aerodynamics (1951) (Dayton, Ohio: Central Air Documents Office).

do we explain the enormous variety displayed by nature in its hydrodynamical phenomena?

Such an "explanation" is not hard to find, since the properties of any hydrodynamical flow depend on many factors other than the driving mechanism. Of these factors, the density, temperature, viscosity, compressibility and thermal conductivity of the fluid are but a few. If the fluid can conduct electricity (and many cosmical fluids, including the earth's core, are good electrical conductors) and magnetic fields are present, the ordinary electromagnetic pondermotive forces due to induced electric currents can, in many circumstances of interest, be very important hydrodynamically. The study of the flow of electrically conducting fluids in the presence of magnetic fields, a very new subject, will be found referred to in the literature as "magneto-hydrodynamics" by some authors and as "hydromagnetics" by others. Its importance in cosmical physics has been frequently emphasised during the past decade, although the subject is not at all well understood at present.

When a body of fluid rotates uniformly as a whole, any hydrodynamical motion to which it may be subject may be influenced profoundly by the ordinary angular momentum requirements. The winds in the atmosphere are controlled very strongly by the "Coriolis forces" due to the earth's rotation although these forces would have a negligible effect on any hydrodynamical motion of the mantle. As we shall see, Coriolis forces cannot be ignored in the core.

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Theoretical Hydrodynamics

Even if, as in the case of the atmosphere, we know the exact conditions to which any particular system is subject, theoretical hydrodynamics is such a rudimentary subject that the complicated way by which any combination of the above-mentioned factors conspires to influence fluid motions can rarely be properly elucidated. The theoretical difficulties impeding progress do not arise in the basic mathematical formulation of the subject. Indeed, we are fairly certain that the mathematical equations need express no more than the laws of classical mechanics, thermodynamics and electromagnetism within almost the whole range of conditions in which we are interested. These equations were formulated long ago. It is because the problems are essentially non-linear that only comparatively few solutions have been obtained, and they were got only when the equations could be linearized, or in particularly simple situations for which the non-linearity could be readily dealt with.

Although "linearized" problems can never yield all the information required, a good deal can be learned from them. A particularly repaying approach to "real" problems has been first to recognize those factors which are likely to be important, and then to obtain insight into their detailed behaviour by constructing and solving a hierarchy of idealized linearized problems, each one made more complicated than the preceding one by successively introducing the factors to be studied. Perhaps the most exhaustive study of this type that has been conducted to date, some of the results of which will be used later, is that of the inhibition of thermal convection in a layer of fluid heated below.

Thermal Convection in a Layer of Fluid Heated Below

It is fairly obvious that in an incompressible inviscid fluid, the heating need only produce an infinitesimal temperature gradient β in order that the lighter fluid

(due to thermal expansion) near the bottom should rise giving place to denser fluid from above. This type of flow is what we mean by "thermal convection", the result of which is a bodily transport of heat upwards.

When we consider a real fluid, viscosity and thermal conduction have to be contended with. Since viscosity impedes fluid motion directly, and since thermal conduction, in attempting to equalize the temperature distribution, reduces the density difference upon which gravity acts to induce motion, and impedes the motion indirectly, the result is that unless β exceeds a finite value, no motion ensues. In a famous paper RAYLEIGH (1916a) deduced that the non-dimensional parameter

$$\frac{g\alpha\beta d^4}{\nu\kappa} \equiv Ra \qquad \ldots.(1.1)$$

determines the behaviour of the fluid, where g is the acceleration of gravity, d the depth of the fluid, ν the kinematical viscosity which is the ratio between the coefficient of ordinary viscosity η and the density ρ, κ is the thermal diffusivity, the ratio between the thermal conductivity χ and the product of ρ and the specific heat at constant pressure c_p, and α is the volume coefficient of thermal expansion. Ra is known as the Rayleigh number. Only when Ra exceeds about 10^3, (the exact value depending on the nature of the boundaries,) does the fluid convect.

RAYLEIGH's original analysis has been extended by several authors (CHANDRASEKHAR, 1952, 1953 and 1954; THOMPSON, 1951) to more complicated situations in which Coriolis forces and magnetohydrodynamic effects have to be taken into account.

When the fluid rotates uniformly at Ω rad/sec about a vertical axis, it is found that the behaviour is determined by Ra and a second parameter, the so-called Taylor number Ta where

$$Ta \equiv 4\Omega^2 d^4/\nu^2. \qquad \ldots.(1.2)$$

When $Ta \to \infty$, the critical value of Ra, Ra_{crit} (say) also tends to infinity, so that the influence of rotation is to inhibit convection at all finite values of β. The value of Ta at which rotation begins to make itself felt, that is, when Ra_{crit} appreciably exceeds the value for $Ta = 0$, is about 10^3.

If the fluid is an electrical conductor, conductivity σ e.m.u. and is situated in a uniform magnetic field, H, parallel to the force of gravity, then a further parameter,

$$Q \equiv \sigma\mu^2 H^2 d^2/\nu^2, \qquad \ldots.(1.3)$$

is required to determine the fluid's behaviour.

When $Ta = 0$, it is found that Ra_{crit} increases indefinitely with increasing Q, although no appreciable alteration in Ra_{crit} arises until Q exceeds about 10^3.

When the motion is influenced by viscous, Coriolis and magneto-hydrodynamic forces the situation becomes a little complicated. However, when viscous forces are not dominant ($Ta > 10^3$, $Q > 10^3$), rotation is more or less influential than the magnetic field according as

$$Ta^{\frac{1}{2}}/Q = (2\Omega\rho/\sigma\mu^2 H^2)^{\frac{1}{2}} \qquad \ldots.(1.4)$$

is greater or less than a number close to unity. As we shall see, this result is of some interest in the case of the core.

Some insight into the subtle way in which various forces interact will repay a careful study of the results of the above-mentioned papers, and in this connection an account of a recent lecture by CHANDRASEKHAR (1953b) deserves attention.

Experimental Hydrodynamics

So far we have only considered theoretical hydrodynamics. The experimental approach to problems in fluid dynamics does not encounter the same type of obstacle as that confronting the theoretician. There are, however, restrictions imposed by the limited range of physical properties of fluids available for experimental work. This can be seen in a fairly simple way if we recall the classical result of REYNOLDS that the character of the flow of a homogeneous incompressible fluid along a straight pipe is determined entirely by the value of the non-dimensional quantity

$$Re \equiv UL/\nu \qquad \ldots.(1.5)$$

where U is a characteristic velocity of flow, L a characteristic length, (identified in this case with the pipe diameter), and Re is the celebrated REYNOLDS number. If we are to simulate motion in a fluid for which $\nu = 10^{-2}$ cm^2/sec, $U = 1$ cm/sec and $L = 10^9$ cm (the size of a sunspot) in a laboratory apparatus for which $U = 1$ cm/sec and $L = 10$ cm a fluid for which $\nu = 10^{-10}$ cm^2/sec would be required. No fluid with such a small coefficient of viscosity is available to the experimenter.

The difficulty of simulating in laboratory models motion occurring in nature in regions of large dimensions is often very serious. However, laboratory investigations can often yield valuable information once the limitations are understood, and in some cases, the *a priori* objections that might be raised against the possibility of performing useful model experiments have proved to be unduly pessimistic. For example, some of the basic features of the general atmospheric circulation have been re-produced in water in the laboratory (FULTZ, 1951; HIDE, In press) and progress in dynamical oceanography is now being made by studying laboratory models (VON ARX, In press).

Turbulence

In conclusion to these general comments, a remark on the subject of hydrodynamical turbulence will be made. Turbulent motion arises when some basic state of laminar flow is unstable, so that the energy of systematic laminar flow is continuously transferred into the energy of more or less random "eddying" motion.

In the case of REYNOLDS' experiments with flow along a straight tube, it was found that the flow is laminar until the value of Re exceeds about 10^3, when it can become turbulent. The instability is due to the velocity shear between the rapidly moving fluid along the axis and the stationary fluid at the walls. REYNOLDS' criterion applies *only* to this simple situation, which is characterized principally by the absence of a pressure gradient across the direction of shear, and cannot, in general, be applied to other cases with even an approximate degree of confidence.

If a fluid system has a characteristic flow velocity U and a characteristic length scale L, we can formally construct a REYNOLDS number Re. In regions of astronomical size Re has enormous values, and for this reason it is often carelessly argued that most fluid motions occurring in nature must be turbulent.

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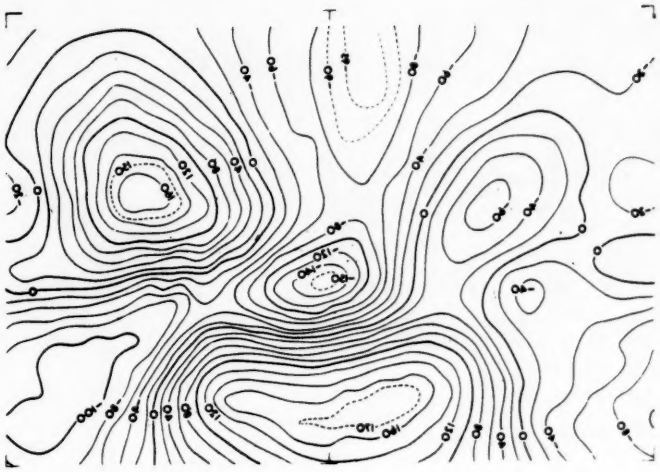

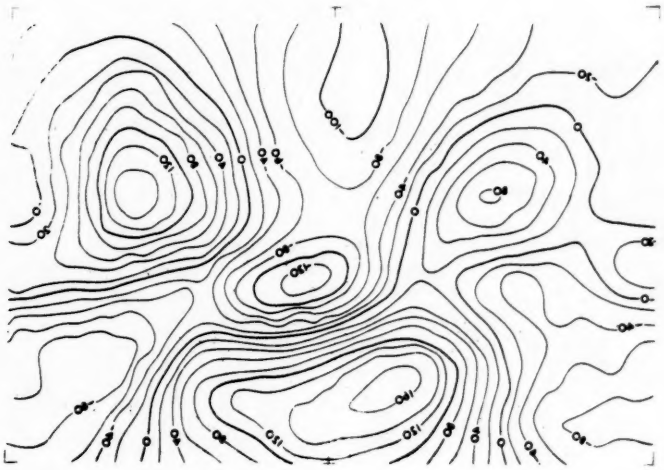

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This, however, need not be the case, and to illustrate that it is improper to base a conclusion that any shearing motion must be turbulent if the REYNOLDS number is large, let us consider a problem in which $\nu = 0$ so that Re is infinite, in which there is a pressure gradient across the direction of shear. This situation obtains in a cylindrical vortex in which the fluid rotates about the axis at Ω rad/sec, where Ω is a function of the radial distance r. The density ρ is taken as uniform. RAYLEIGH (1916b) showed nearly forty years ago that the laminar zonal motion would be stable or unstable according as the quantity

$$\frac{d}{dr}(r^2\Omega(r)) \gtrless 0. \qquad \ldots.(1.6)$$

The quantity on the left hand side of this criterion is just the rate at which the angular momentum increases with increasing r, apart from a factor ρ. There is a definite analogy between this quantity and β, the temperature gradient in the problem of thermal convection, and indeed, this is no mere mathematical analogy; there is a close physical similarity between the two cases.

A particularly interesting application of the above criterion would be to an angular velocity distribution given by KEPLER's Law, $\Omega^2 r^3$ equal to a constant. Such a vortex would be stable, as would all vortices for which Ω is proportional to r^n if $n < -2$.

As in the case of thermal convection, modifications of the criterion (1.6) arise when we include the effects of viscosity and magneto-hydrodynamic forces. The influence of these factors has been studied by several authors (TAYLOR, 1923b; MEKSYN, 1946; CHANDRASEKHAR, 1953c, MICHAEL, 1954) following RAYLEIGH's original contribution.

2. THE EARTH'S INTERIOR

No claim to completeness is made for this section. Two standard treatises (JEFFREYS, 1952; GUTENBERG, 1951) on the earth's interior have appeared recently, and the subject is discussed in detail in other chapters of this book.

The earth is a nearly spherical body of radius $R_s = 6371$ km. Radioactive dating measurements on the oldest rocks put its age at somewhat greater than 4×10^9 years. The circumstances of its birth are obscure.

From the value of the force of gravity at its surface, it is found that the mean density of the earth is 5·5 g/cm^3. Since we know from measurements of the precession of the equinoxes that the moment of inertia is about 15 per cent less than the value corresponding to a uniform density distribution, the earth must be centrally condensed.

By far the most powerful method for studying the earth's interior is afforded by seismology, the study of sound waves generated by earthquakes. Earthquake waves can penetrate to great depths within the earth. On detection at the surface they bring with them information about the mechanical properties of the material through which they have travelled.

The two most important types of seismic wave are the so-called P (primary) and S (secondary) waves. In the P wave the induced particle displacement is longitudinal, that is, parallel to the direction of wave propagation. P waves can be transmitted by any type of compressible medium, solid, liquid or gaseous. In the S wave the particle displacement is transverse to the direction of wave

propagation, so that the medium undergoes geometrical deformation. Since gases and liquids do not resist deformation, only solids (materials having rigidity) can transmit S waves.

Seismic data combined with the values of the mean density and moment of inertia of the earth reveal the following facts about its interior.

The outer crust of the earth is very thin, only some 35 km. Its properties will not concern us here. Below this level, the composition of the earth depends

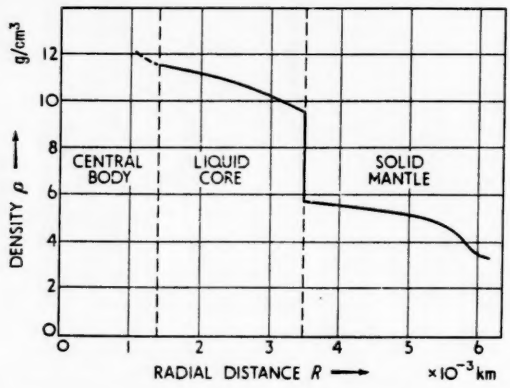

Fig. 1. Density ρ as a function of radial distance R within the earth.

only on R, the distance from the centre. The density ρ (see Fig. 1) increases continuously and monotonically from 3·3 g/cm³ to 5·7 g/cm³ at $R = 3473 \pm 4$ km. Within this region, which is known as the mantle, both P and S waves are transmitted, hence, at least to short period forces such as are associated with sound waves, the mantle behaves as a solid.

At $R = 3473$ km, ρ experiences an abrupt change from 5·7 to 9·5 g/cm³. This is the LEHMANN-GUTENBERG discontinuity, below which ρ increases continuously to its central value of about 12 g/cm³. There is some evidence for a discontinuity in $d\rho/dR$ at $R = 1400$ km. The region below the LEHMANN-GUTENBERG discontinuity is known as the core, and the region below $R = 1400$ km as the central body.

Although P waves penetrate the core without suffering much damping, no S wave that has passed right through it has ever been positively identified, and it has thus been inferred that the core is a liquid, a conclusion firmly supported by other kinds of geophysical data (JEFFREYS, 1952). Our knowledge of the central body is fairly vague. BULLEN believes that it might be solid (BULLEN, 1946).

Seismic data alone do not betray the chemical composition of the earth. However, combined with a knowledge of relative chemical abundances they have led to the following picture:

The mantle is probably composed of the mineral olivine, a ferro-magnesium silicate of composition (MgOFeO) SiO_2 where Mg and Fe are freely substitutable. The range is from forsterite, $(MgO)_2\,SiO_2$ to fayalite $(FeO)_2\,SiO_2$ whose respective densities are 3·19 and 4·14 g/cm³ at ordinary pressures.

Since iron is an abundant element whose density agrees with that of the core at the pressures prevailing there, most geophysicists believe that the core is composed mainly of this element. Complete agreement on this point has not been reached; in particular, the suggestion that the core consists of a high pressure modification of olivine is receiving attention at present (JEFFREYS, 1952).

The temperature within the earth has been fairly extensively studied (JEFFREYS, 1952; GUTENBERG, 1951; BULLEN, 1946). JEFFREYS (1952) takes a model in which the core is in convective equilibrium (and hence the temperature has

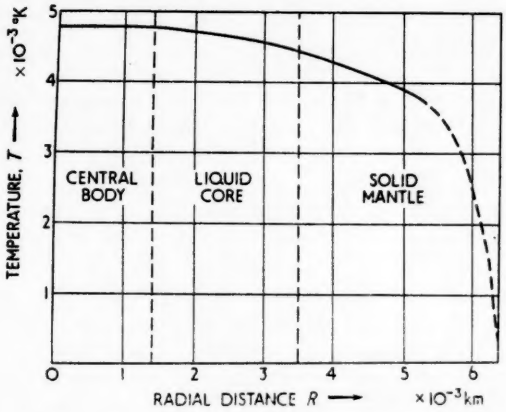

Fig. 2. Temperature T as a function of radial distance R within the earth, according to JACOBS.

the adiabatic value) and the mantle is everywhere at the melting point corresponding to the particular pressure. JEFFREYS's model has not been seriously challenged. The adiabatic gradient is given by the formula

$$\left(\frac{dT}{dR}\right)_a = -\frac{g\alpha T}{J_0 c_p} \qquad \ldots.(2.1)$$

and the melting point gradient by

$$\left(\frac{dT}{dR}\right)_m = -\frac{gT}{J_0 L_0}\left(\frac{\Delta\rho}{\rho}\right)_m \qquad \ldots.(2.2)$$

where T denotes the temperature, J_0 the mechanical equivalent of heat, L_0 the latent heat of fusion, $(\Delta\rho/\rho)_m$ the fractional density change at fusion and the other quantities are as defined previously.

If we accept the JEFFREYS model, the uncertainty in the temperature distribution is due entirely to a lack of accurate estimates of the quantities involved in the last two expressions. The earliest estimates that were made yielded values for (dT/dR) in the mantle of 5 falling with depth to 2°C/km and a mean value of about 1°C/km in the core, implying a central temperature of somewhat less than 10,000°C. JACOBS (1952) has rediscussed the problem quite recently basing his results on the assumption that α^{-1} varies linearly with pressure. The temperature distribution thus emerging is plotted in Fig. 2. These results have been adopted by BULLARD (BULLARD and GELLMAN, 1954) in his most recent paper. It is seen from this diagram that T rises from 3600°K at $R = 5400$ km to 4350°K

at the core surface, the gradient slackening as we proceed inwards. The temperature continues to increase within the core until 4800°K is reached at the centre.

The principal specific heats, c_p and c_v, of the mantle have been put at about 0·3 cal/g°C by BIRCH (1952), the variation with R being slight. BULLARD (1950) has given their values for the core, namely, 0·18 and 0·16 cal/g°C respectively.

The volume coefficient of thermal expansion α has been estimated by several authors. BIRCH (1952) states that $\alpha = 10^{-5}$/°C in the mantle, the uncertainty increasing with depth. JACOBS's (1952) hypothesis (see above) implies that α decreases from $3{\cdot}6 \times 10^{-5}$/°C at the depth of 200 km to 9×10^{-6}/°C at the surface of the core. BULLARD gives $\alpha = 9 \times 10^{-6}$/°C for the core in one of his earlier papers (BULLARD, 1950) but adopts a somewhat smaller value $\alpha = 4{\cdot}5 \times 10^{-6}$/°C in his most recent work (BULLARD and GELLMAN, 1954).

Although olivine, (of which the mantle is mainly composed), is a fairly good electrical insulator at ordinary pressures and temperatures, it behaves at laboratory pressures like a typical semiconductor for which σ increases fairly rapidly with temperature. Hence, unless high pressures tend to suppress semiconduction to any significant extent, the mantle is expected to have an appreciable value of σ.

It is known from the study of electric currents induced in the earth by the changing currents in the ionosphere that σ increases rapidly in the first 700 km to a value of 10^{-11} e.m.u. (LAHIRI and PRICE, 1938). HUGHES and RUNCORN (HUGHES, 1953) have examined the variation of σ throughout the whole mantle in terms of a semiconduction hypothesis. Their results indicate that σ rises to about 10^{-8} or 10^{-9} e.m.u. near the core-mantle boundary.

Since the core is probably metallic, σ there is expected to be fairly high. Based on the assumption that the core is composed mainly of iron, several estimates of σ have been made. BULLARD (1949b; 1954) adopts $\sigma = 3 \times 10^{-6}$ e.m.u., stating that this value is probably uncertain by a factor of three.

The thermal conductivity, χ, of olivine under ordinary conditions is $1{\cdot}2 \times 10^{-2}$ cal/(cm-sec-°C). Its variation with pressure and temperature is not accurately known, although ELSASSER (1950b) suggests that χ increases with pressure and theory indicates that it should decrease with temperature.

Employing the WIEDEMANN-FRANZ law connecting χ with σ and T for a metal, BULLARD (1950; BULLARD and GELLMAN, 1954) estimates χ to be 0·1 cal/cm- sec-°C for the core; the uncertainty in this estimate may be as large as a factor of five.

Although the mantle is a solid from a seismic point of view, slowly varying forces can produce deformation. HASKELL (1936) and MEINESZ (VENING-MEINESZ, 1937) have argued that the mantle has a coefficient of kinematical viscosity ν of about 10^{22} cm^2/sec in its upper reaches.

BULLARD (1948) and INGLIS (1941) have made instructed guesses at ν of the core, both arriving at $\nu = 10^{-3}$ cm^2/sec, one tenth that of water. JEFFREYS (1952) has shown that the fact that P waves in the core are not appreciably damped implies that ν cannot exceed a certain value. BENIOFF (GUTENBERG 1951) pointed out that the calculation on which JEFFREYS' result is based underestimates this upper limit to ν, which is about 10^9 cm^2/sec. Thus, the most that can be concluded about this quantity is that $10^{-3} < \nu \ll 10^9$ cm^2/sec.

The results of this section are summarized in Table I.

Table I. Some Physical Properties of the Earth's Interior

	Liquid Core	*Solid Mantle*
Density ρ g/cm^3	9·7 at surface rising to 11·5 at centre	3·3 at 35 km depth rising to 5·7 near core (i.e. at R = 3473 km)
Temperature T°C	4800 at centre 4350 at surface	3600 at R = 5400 km 4350 at R = 3473 km
Temperature gradient $\frac{dT}{dR}$ °C/km	Adiabatic 0·13 (mean)	Melting point 1·0 (mean)
Principal specific heats c_p and c_v cal/g°C	$c_p = 0{\cdot}18$ $c_v = 0{\cdot}16$ uncertain by 30%	c_p, $c_v \approx 0{\cdot}3$, uncertain by 30%
Thermal conductivity χ cal/cm sec°C	0·1 uncertain by factor of 5	0·012 uncertainty unknown
Volume coefficient of thermal expansion α°C^{-1}	$4{\cdot}5 \times 10^{-6}$ uncertain by 30%	10^{-5}
Electrical conductivity σ e.m.u.	3×10^{-6} uncertain by 30%	10^{-11} at 700 km depth^{-8} rising to between 10^{-8} and 10^{-9} near core
Coefficient of kinematical viscosity ν cm^3/sec	Uncertain, but $10^{-3} < \nu \ll 10^9$	10^{22} near top of mantle

3. THE EARTH'S MAGNETIC FIELD

The earth has a magnetic field which originates mainly from within, and of which no entirely adequate explanation has been given.

Description and Analysis

A general magnetic field distribution on the surface of a sphere could be due to sources within the sphere, sources outside the sphere, and to currents crossing the surface. The first two such contributions in the case of the earth give rise to what are usually termed the "internal" and "external" components. They can be derived from a scalar potential, unlike the third component which is therefore termed the "non-potential" field.

The separation of the earth's field into its internal and external components is achieved by spherical harmonic analysis (CHAPMAN and BARTELS, 1940). The line integral of the horizontal field around a closed loop, which would vanish in the absence of a "non-potential" component, is a measure of the strength of electric currents cutting the surface. Errors in such analyses result from the lack of adequate data, especially from the vast unpopulated areas of the earth's surface.

The first spherical harmonic analysis of the earth's field was performed by GAUSS in 1838, repetitions of which have since been made, notably by SABINE, SCHUSTER and CHAPMAN. The most comprehensive one to date is due to VESTINE and his collaborators, who analysed all the available data since magnetic measurements were first made several centuries ago (VESTINE *et al.*, 1947b).

The most notable feature of this work is the result that the earth's field is of internal origin (which was suggested as long ago as 1600 by GILBERT), the apparent contribution due to external sources being so small that it is not definitely significant within the errors involved. VESTINE's search for a non-potential field failed to discover any significant contribution due to currents crossing the surface.

By spherical harmonic analysis the field due to internal sources is referred to hypothetical multipole sources located at the earth's centre. The lowest order multipole is the dipole, which has three components, that along the earth's rotation axis (the axial dipole) and two mutually perpendicular dipoles lying in the equatorial plane. Next come the quadrupoles, five in number, and so on. In Table II the major results of VESTINE's analysis of the main field of 1945 are

Table II. Vestine's Spherical Harmonic Analysis of the Earth's Magnetic Field for 1945. (*Unit:* 10^{-4} *gauss*)

Axial Dipole Component	Equatorial Dipole Components	Quadrupole Components
− 3057	− 211	− 127
	+ 581	+ 296
		− 166
		+ 164
		+ 54

given (VESTINE *et al.*, 1947b). The most striking feature is the vast preponderance of the axial dipole over the equatorial dipole and quadrupole components. The strengths of multipoles of higher degree than quadrupole are quite small, the spherical harmonic series showing rapid convergence.

The near coincidence between the geographic and geomagnetic axes during the few centuries since the invention of the magnetic compass is an arresting result. We shall see later that this is not a temporary feature of the field, but is a very fundamental average property.

The Secular Variation

The strength of the earth's magnetic field and its geographical distribution are not independent of time. In 1635 GELLIBRAND made an important discovery when he noted that the magnetic meridian at London moved from its orientation 11·3° east of true north in 1580 to 4·1° east of true north in 1634. It is now known that all the magnetic elements undergo these large secular changes.

VESTINE *et al.* (1947a) have analysed the secular variation of the geomagnetic field that occurred during the period 1905–45. They computed change of each magnetic element during ten year intervals and then analysed the time derivative in the same way that the field itself is analysed.

Figs. 3 and 4 are included to illustrate the secular variation. Figs. 3a, b, give the non-dipole field, (i.e. the total less the dipole part of the field), in 1945 and 1907·5 respectively. The contours are lines of equal vertical magnetic force, and the arrows give the horizontal force.

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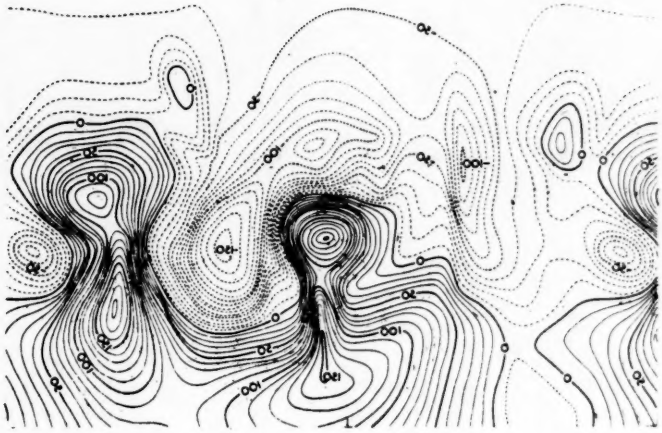

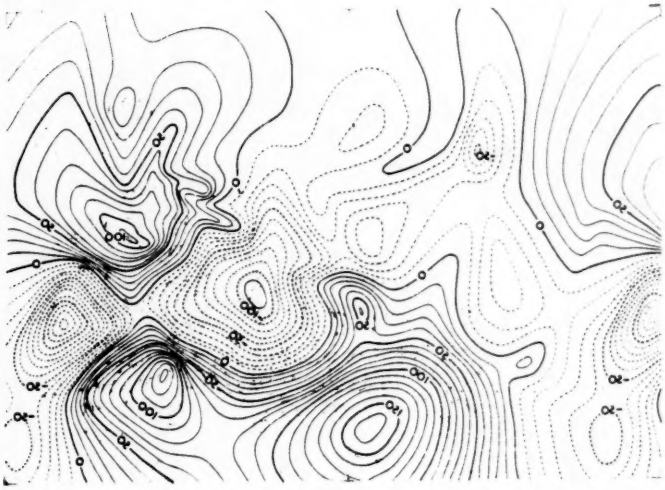

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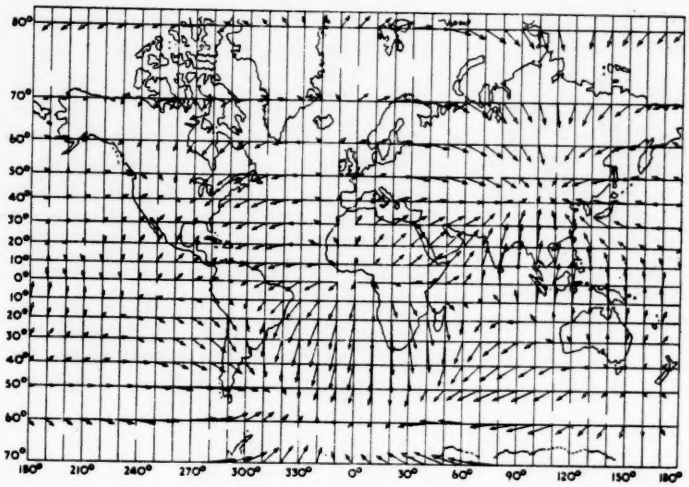

Fig. 3 (a). Non-dipole field for 1945. The contours give the vertical field at intervals of 0·02 gauss. The arrows give the horizontal component, an arrow 9·3 mm long represents 0·1 gauss.

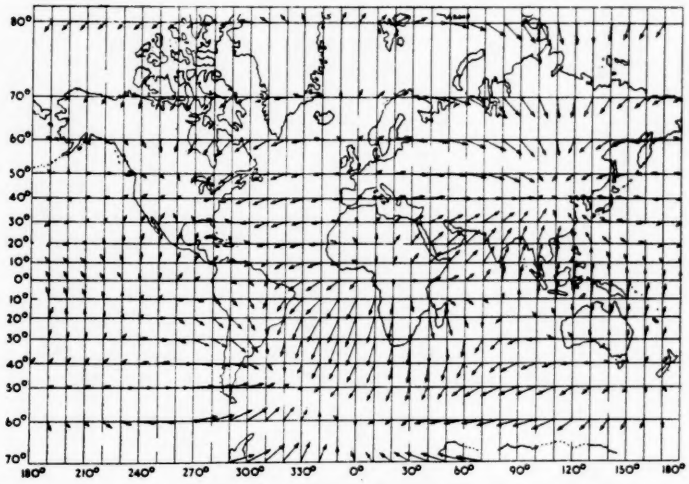

Fig. 3 (b). Non-dipole field for 1907·5. The contours give the vertical field at intervals of 0·02 gauss. The arrows give the horizontal component, an arrow 9·3 mm long represents 0·1 gauss.

By comparing these two maps, we discover that not only did the general form of the non-dipole field change slightly (but noticeably) during the time interval represented, but a westward drift of the whole magnetic pattern occurred. The latter feature can be readily recognized by comparing the positions of the centres of the oval curves.

VESTINE *et al.* (1947a), during the course of their study of the secular variation, prepared maps of the time derivative of the magnetic elements at various epochs. Two such maps, for 1912·5 and 1942·5, giving the change in vertical force that occurred during the ten year periods centred on these dates, are reproduced in Fig. 4. The curves of equal change are termed "isopors" and the centres of active regions "isoporic foci". A westward drift of the secular variation field will be recognized from these two maps. BULLARD *et al.* (BULLARD and GELLMAN, 1954), have examined the properties of the drift motion of the non-dipole field and the secular variation field. The result of the foregoing investigations was the discovery of the following properties of the secular variation and non-dipole field:

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(a) The secular variation field is of internal origin.

(b) Unlike the field itself, the secular changes have only a small dipole component, that is to say, it is the non-dipole field that undergoes the most rapid change.

(c) On typical magnetic maps, lines of equal annual change of any element (isopors), at any epoch, form a series of oval curves surrounding points at which the changes are most rapid (isoporic foci).

(d) At any epoch the sets of isopors cover areas of continental size and are separated by regions over which the changes are small.

(e) The regions of rapid change, of which there are about a dozen at any one time, may alter considerably in form in the course of only a few decades, and active areas may establish themselves during that time.

(f) The non-dipole field and the secular variation exhibit a general drift relative to the earth's surface, which is mainly westward. BULLARD's *et al.*'s (1950) analysis of VESTINE *et al.*'s (1947a) data reveals that between 1907·5 and 1945, the secular variation field drifted westward at a mean rate of $0{\cdot}32 \pm 0{\cdot}067$ degrees of longitude per year, and the non-dipole field at $0{\cdot}18 \pm 0{\cdot}015$ degrees of longitude per year. The apparent difference between these two rates could not be conclusively established as significant, nor could the apparent north-south motion and the variation of westward drift with latitude be shown to be real, due to the errors involved.

The study of the secular variation in terms of the spherical harmonic coefficients of the rate of change of the field is not a satisfactory procedure since there is no preponderant term and the series converges quite slowly. Indeed, even in the case of the field itself, with its predominant dipole, spherical harmonic analysis, in referring the field to hypothetical geocentric multipoles, fails to reveal the actual location and nature of the physical processes involved. Hence the value of this type of analysis is rather limited, the limitation being more serious in the case of the secular variation than in the case of the field itself.

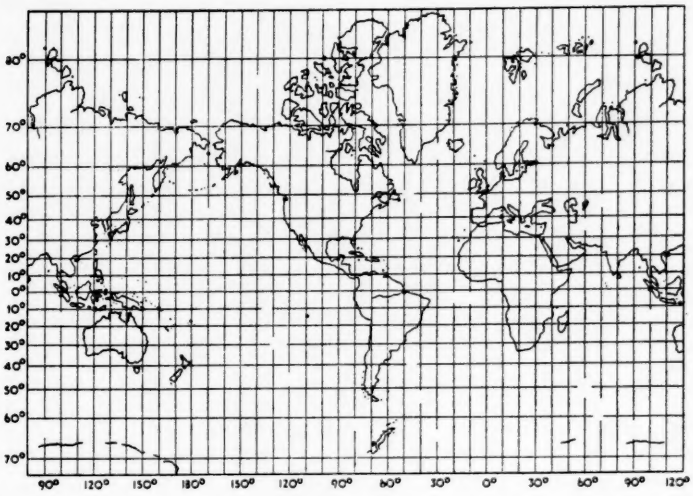

Fig. 4 (a). Geomagnetic secular change in gammas per year, vertical intensity, epoch 1912·5.

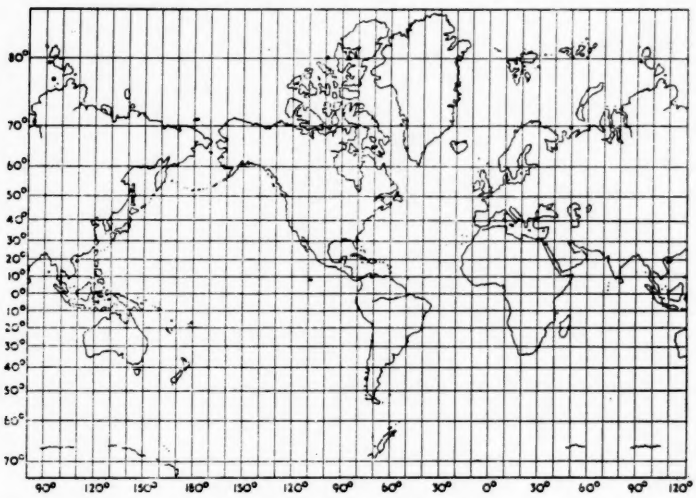

Fig. 4 (b). Geomagnetic secular change in gammas per year, vertical intensity, epoch 1942·5.

Several investigators have recognized this fact and have made more realistic secular variation analyses which lead to tentative physical interpretations, (BULLARD, 1948; MCNISH, 1940; LOWES and RUNCORN, 1951) which cannot, however, be described here.

Rock Magnetism

Most of our knowledge of the earth's magnetism comes from direct magnetic observations. Since such measurements go back only a century or so, (a minute fraction of the age of the earth) it is fairly clear that no entirely adequate formulation of the geomagnetic problem can be made until our knowledge is enlarged by an enquiry into the history of the phenomenon during various geological epochs. Such an enquiry was initiated only quite recently when investigators began to study the magnetic properties of rocks.

The underlying assumption upon which the history of geomagnetism is translated from the magnetic properties of rocks is that the direction of magnetization of certain rocks represents the direction of the geomagnetic field at some remote time, having been "fossilized" due to the high coercive force of the material, after some process magnetized the rock in the first place.

Measurements made on rocks of Tertiary and Quaternary age suggest that the earth's field has been mainly that of an axial dipole for at least the last few millions of years, and the present displacement between magnetic and true north is a merely transient effect (TORRESON *et al.*, 1949; HOSPERS, 1952). A more startling suggestion based on further measurements of rocks of the same geological periods is that although the geomagnetic dipole was always axial, it did not always have the same polarity (HOSPERS, 1952; BRUCKSHAW and ROBERTSON, 1949). Several such "reversals" apparently occurred during the Tertiary and Quaternary; each was accomplished in about 5000 years and persisted for about 25,000 years. (The last figures are only claimed to be very approximate and may be uncertain by a factor of ten).

Recent polarization measurements of rocks which were laid down during many geological epochs going back as far as the Precambrian do not admit of immediate interpretation in terms of the single hypothesis that the earth's field was always nearly that of an axial dipole with the earth's rotation axis in its present geographical position. However, there is no compelling evidence that the hypothesis must be abandoned, since these rock magnetism data appear to be explicable if a simple extra hypothesis concerning the wandering of the geographic poles relative to the earth's surface is made (RUNCORN, 1955). Uncertainty on this point should be reduced when experiments still in progress have been completed.

Theories of the Earth's Magnetism

Any theory of the earth's magnetism must explain a predominantly axial dipole field of about 0·5 gauss at the earth's surface, corresponding to a dipole moment of 8×10^{25} e.m.u. It must also account for the relatively small but quite significant non-dipole field, and be sufficiently flexible to allow for an explanation of the secular changes.

Although the suggestion that the polarity of the main dipole occasionally reverses has yet to be completely confirmed, the evidence is now so strong that

it may be unwise to ignore it in formulating the requirements of a geomagnetic theory.

It is scarcely necessary to add that whatever mechanism might be proposed, it cannot be accepted unless it is capable of operating under the conditions that prevail within the earth.

Historically, the space and time variation of the field have been described separately, so that there was a tendency for early attempts to provide a theory to ignore the secular variation. Perhaps the most notable feature of more recent investigations has been the recognition of the secular variation as an essential part of the whole phenomenon, and that not only is the separation of the space and time properties of the field no logical convenience, but may well be a misleading procedure.

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Theories that were advanced before about fifteen years ago are reviewed in two standard works (CHAPMAN and BARTELS, 1940; FLEMING, 1939). The suggestions that the field is due to permanent magnetism, electrostatic changes or gyromagnetic effects are untenable for a variety of reasons, the main one of which is that none of these causes could account for more than very tiny field strengths.

A recent suggestion of BLACKETT's has received some attention of late. BLACKETT (1947) noted that, very roughly, the magnetic moments of the earth, the sun, and of a certain star are proportional to their respective angular momenta of rotation, and proposed that a general magnetic field is a fundamental property of a massive rotating body.

BLACKETT's hypothesis implies that there should be a very minute field associated with a massive body in the laboratory due to the rotation of the earth. However, he failed to detect such an effect with the sensitive apparatus he devised (BLACKETT, 1952).

A further test was proposed by BULLARD. If the earth's magnetic field is due to a mechanism located at great depths, the radial variation of the field near the surface would be such that both the horizontal and vertical components increase with depth. On BLACKETT's hypothesis, however, in which every part of the earth contributes to the field, the horizontal component is expected to decrease with depth. RUNCORN and his collaborators (RUNCORN *et al.*, 1951), from measurements made in coal mines, found that the radial variation indicates a deep-seated origin of the field, and that their results cannot be reconciled with BLACKETT's suggestion.

It might be added that despite the inadequacy of BLACKETT's proposal, the renewed interest in geomagnetism that it stimulated was very considerable.

Electric Currents within the Earth

As far as can be seen, the only remaining possibility is that the geomagnetic field is due to ordinary electric currents circulating within the earth. LAMB (1883) showed long ago that freely decaying currents in a sphere of radius R would, due to electrical resistance, be reduced to e^{-1} of their initial strength in a time not longer than $4\sigma R^2/\pi$. This time in the case of the earth, which can be calculated roughly from the data of Table I, is only about 10^5 years, much less than 4×10^9 years which is the age of the earth. Since rock magnetism data indicate that the strength of the field was much the same in the past as it is now, the field cannot be freely decaying. Hence, there must be a mechanism within

the earth that continuously regenerates these currents against the agency of Joule heating.

It is fairly natural to suppose that the generation takes place in that region in which the currents experience least resistance, and in view of the conductivity data of Table I, this region is the core. That the core is the seat of geomagnetic activity is supported by the following consideration due to BULLARD (1948) and others. The time scale of the secular variation is singularly small, only a few decades, when we consider that geological processes arising in the solid parts of the earth take millions of years. However, if we suppose that the liquid core sustains hydrodynamical motion, which is in some way responsible for the earth's magnetism, then the rapidity of the secular variation should not be hard to account for.

An axial dipole moment of 8×10^{25} gauss cm^3 could be produced by a uniform zonal electric current of density $j = 2 \times 10^{-7}$ e.m.u. corresponding to a total current of 5×10^8 e.m.u. or 5×10^9 A. By Ohm's law, an electric field $E = j/\sigma = 7 \times 10^{-2}$ e.m.u. or 7×10^{-10} V/cm is implied, corresponding to an electromotive force of only 0·1 V over a distance comparable with the core radius.

Electrical resistance would produce a Joule heating of $j^2/\sigma = 1{\cdot}3 \times 10^{-8}$ erg/cm^3 sec or 5×10^{10} cal/sec for the whole core. The last figure should be compared with the heat flow at the earth's surface from radioactive sources in the crust of 3×10^{14} cal/sec and the 10^{19} cal/sec of solar radiation reaching the earth. It was concluded, therefore, that there would be nothing unreasonable about postulating the existence of these currents.

Although zonal electric currents produce a magnetic field that has lines of force which cut the earth's surface, there are current configurations that produce magnetic fields not possessing this property. Such fields will be termed "contained" fields. One example would be the zonal magnetic field due to an electric current flow restricted to meridian planes. Since contained fields do not contribute to the magnetic field we measure at the surface, the strength of the electric currents in the core may exceed the value of 5×10^9 A given above. As we shall see, it is now fairly certain that there are strong contained fields within the earth.

Although no one has discovered an entirely acceptable mechanism for generating electric currents in the core, two interesting suggestions have been made which give rise to the so-called "thermoelectric" and "dynamo" theories of the earth's magnetism.

The "Thermoelectric" Hypothesis

The proposal that thermoelectric currents circulate within the earth was first made by ELSASSER in 1939, and this idea has been pursued, with modifications, by RUNCORN (1954). Thermoelectric electromotive forces are generated whenever two materials with different electrical properties are in contact at points which are at different temperatures. In ELSASSER's mechanism, the thermo-e.m.f.'s are supposed to be due to inhomogeneities in the core material created and continuously regenerated by "turbulent convective fluid motion" within the core. RUNCORN, on the other hand, proposes that such e.m.f.'s arise at the interface between the core and the mantle where we have a surface of contact between materials which differ in their electrical properties. Temperature

differences between different parts of the core-mantle interface may be due to the eccentricity of the earth and to thermal convection in the core.

Of the total current generated by ELSASSER's process only a small fraction would be responsible for the surface magnetic field, the greater part producing only a contained field. All the thermoelectric currents generated by RUNCORN's mechanism would produce contained fields, and, to complete the process, an appeal is made to inductive interaction between these fields and the hydrodynamical flow in the core.

Although it appears fairly reasonable to expect that the core is in hydrodynamical motion, as we shall see in the next section, that this flow is thermally induced is not established.

Since the thermoelectric power of materials under the conditions prevailing in the core is unknown, a quantitative examination of the thermoelectric theory is out of the question at present. If the thermoelectric power of the core-mantle combination is 100 μV/°C, RUNCORN shows that temperature fluctuations of more than 10°C on the core-mantle boundary would be required. Similar values are required by ELSASSER. If the heat transport by convection is the same in all directions and the temperature field on a level surface (in particular, the core-mantle interface) is due entirely to core motions, then, as INGLIS and TELLER (1940) have pointed out, the convective heat flow implied by the thermoelectric hypothesis would be excessive. If H_c is the convective heat flow in calories per second,

$$H_c = 2\pi \bar{R}^2 f \rho c_p \bar{U}_R \Delta T_\phi \qquad \ldots.(3.1)$$

where $\bar{U}_R$ is the mean value of the radial velocity of flow, $\bar{R}$ is the mean radius of the core, ΔT_ϕ is the temperature difference between rising and falling streams and f is a factor less than unity to allow for the possibility that not all the core material participates in the motion. If we identify ΔT_ϕ with the 10°C required to produce sufficiently powerful thermoelectric currents and suppose that $H_c < 3 \times 10^{14}$ cal/sec, the heat flow through the earth's surface, we find on employing the data of Table I that $f\bar{U}_R < 10^{-7}$ cm/sec. Since it is unlikely that f could be less than 10^{-1} and $\bar{U}_R$ is probably a good deal greater than 10^{-6} cm/sec (see Section 4), it follows that H_c implied by equation (3.1) would greatly exceed that due to radioactive sources in the earth's crust. This is the basis of the objection raised by INGLIS and TELLER.

The foregoing calculation would have to be modified if thermal convection is more or less powerful, say, in directions parallel to the earth's rotation axis than in directions at right angles. We shall see later that the earth's rotation probably introduces an asymmetry of motion of this type.

A further modification would arise if the eccentricity of the earth produces a significant temperature contrast between the pole and equator at the core-mantle interface even in the absence of convection. In the absence of any knowledge of the heat source distribution in the core, the most that can be said at present is that the aforementioned modifications of the heat flow calculations would reduce the severity of the heat flow objection to the thermoelectric theory by an amount that remains to be estimated.

It might be added that RUNCORN (1954) has, in adducing evidence that primary sources of electric currents are to be found at the core-mantle interface, made an important point that might be taken to support the thermoelectric theory.

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The "Dynamo" Theory

This theory, the principal proponents of which are BULLARD and ELSASSER, has been developed to a far greater extent than any other. It is based on the principle of the ordinary homopolar, or self-exciting, dynamo, the action of which may be illustrated as follows: A copper disk (see Fig. 5) radius a_0 cm is rotated on an axle at Ω_0 rad/sec by applying a torque to the axle from an external agency. If a slight magnetic field ΔH_0 which cuts the disk normally is applied from

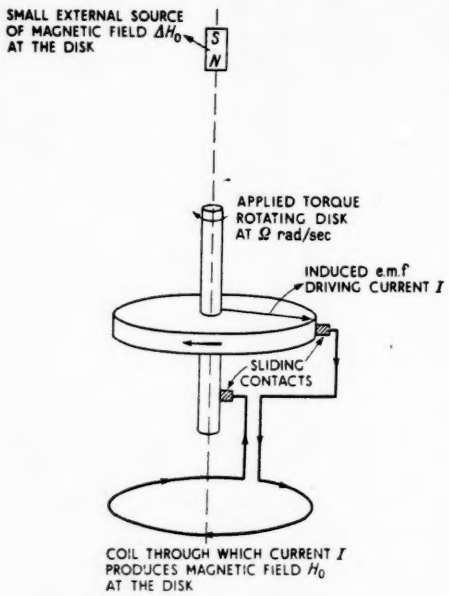

Fig. 5. Homopolar dynamo.

outside (perhaps by placing a weak magnet in the neighbourhood) then initially an electromotive force $\frac{1}{2}\Delta H_0/a_0{}^2\Omega_0$ is developed between the axle and the periphery of the disk. This drives a current I around the coil connected by sliding contacts across the disk, and if the coil is wound in the right sense, the field $2\pi I/a_0 = H_0$ (say) produced at the disk is such as to increase the inducing field to $H_0 + \Delta H_0$, which, in its turn, increases the e.m.f. across the disk to $\frac{1}{2}a_0{}^2\Omega_0(\mathrm{H}_0 + \Delta H_0)$. However, this induced e.m.f. is offset by the voltage drop $R_0 I$ across the resistance of the circuit, R_0, and the back e.m.f. $\pi a_0{}^2\,(\mathrm{d}H_0/\mathrm{d}t)$ due to the fact that the flux through the disk is changing with time. Thus, since we are assuming that the magnetic field is amplified, and ΔH_0 may be made infinitely small,

$$\tfrac{1}{2}a_0{}^2\Omega_0 H_0 = R_0 I + \pi a_0{}^2 \frac{\mathrm{d}H_0}{\mathrm{d}t}, \qquad \ldots.(3.2)$$

or, on substituting $I = a_0 H_0/2\pi$ (approximately) and rearranging,

$$2\pi^2 a_0{}^2 \frac{\mathrm{d}H_0}{\mathrm{d}t} = H_0(\pi\Omega_0 a_0{}^2 - R_0). \qquad \ldots.(3.3)$$

From the last equation, it is seen that in order that H_0 should increase with time

$$\pi\Omega_0 a_0 > R_0 \quad \ldots.(3.4)$$

(and if a steady state is to be produced, $\pi\Omega_0 a_0 = R_0$).

In our mechanism, we have assumed that Ω_0 is constant. This implies that the applied torque is sufficient to balance the mechanical reaction due to the interaction between the currents and the magnetic field, and to provide the energy required to increase the magnetic field. The device is essentially a mechanism for converting mechanical energy into magnetic energy, and since the circuit has finite resistance, some of the input energy is wasted in the form of Joule heating. In a self-exciting dynamo, provided we have a small inducing field ΔH_0, the value of ΔH_0 becomes unimportant once the amplification has got under way. The criterion (3.4) essentially states that the kinetic energy of the system must be large enough to supply the Joule heating with some left over to feed into the magnetic field.

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In a series of papers BULLARD (1948; 1949; 1950; BULLARD and GELLMAN, 1954; BULLARD *et al.*, 1950) and ELSASSER (1946; 1947; 1950a) have independently examined the possibility that inductive interaction between hydrodynamical motion in the earth's core (analogous to the rotation of the disk) and some small adventitious field (ΔH_0) can produce the electrical currents responsible for the earth's magnetism. Essentially, the suggestion is that the energy of the magnetic field is ultimately derived from whatever energy source drives the fluid motion (see Section 4) through the intermediate stage of inductive interaction. An earlier suggestion of this kind was made by LARMOR (1919) in an attempt to explain the general solar magnetic field.

Before discussing the dynamo theory in detail, it is necessary to examine roughly how large we might expect electromagnetically induced e.m.f.'s to be in the core. If a conductor moves relative to a magnetic field of strength H gauss in a medium of permeability μ at v cm/sec, the induced electromotive force is $\mu v H$ e.m.f. We have already seen that e.m.f.'s of about 10^{-1} e.m.u. are required, and if $\mu = 1$ and $H = 1$ gauss, $v = 10^{-1}$ cm/sec. The westward drift of the geomagnetic field corresponds to a linear velocity of this magnitude, and therefore if we interpret the secular variation as a manifestation of hydrodynamical flow in the core, it appears that inductive processes in the core would be very powerful. Whether they could generate the field at the surface is a matter for detailed study, but it was through the above order of magnitude calculation that the authors of the dynamo theory recognized that such a study was worth pursuing.

The development of the dynamo theory is confronted with two major problems. First, it is necessary to show that it is possible to devise some configuration of hydrodynamical flow that is capable of producing a (mainly) axial dipole field. And second, it must be shown that this flow exists in the core. The first of these problems has been examined in detail, without entirely conclusive results. The second has not been attempted to date.

To illustrate the procedure that was employed, let us consider the electromagnetic equations appropriate to the problem in hand. These are

$$\nabla \times \boldsymbol{H} = 4\pi \boldsymbol{j}, \quad \ldots.(3.5)$$

$$\nabla \times \boldsymbol{E} = -\mu \frac{\partial \boldsymbol{H}}{\partial t}, \quad \ldots.(3.6)$$

$$\nabla \cdot \boldsymbol{H} = 0, \qquad \ldots.(3.7)$$

and

$$\boldsymbol{j} = \sigma[\boldsymbol{E} + \mu \boldsymbol{u} \times \boldsymbol{H}], \qquad \ldots.(3.8)$$

where $\boldsymbol{H}$ denotes the magnetic field, $\boldsymbol{E}$ the electric field, $\boldsymbol{u}$ the velocity of the conducting fluid at a point in space, $\boldsymbol{j}$ the current density, and μ and σ are taken as constant. Electromagnetic units are employed throughout. In equation (3.5) the displacement current is ignored, a legitimate procedure when the speeds involved are much less than the speed of light. On eliminating $\boldsymbol{E}$ and $\boldsymbol{j}$ between the last few equations it is readily shown that

$$\frac{\partial \boldsymbol{H}}{\partial t} = \frac{1}{4\pi\mu\sigma} \nabla^2 \boldsymbol{H} + \nabla \times (\boldsymbol{u} \times \boldsymbol{H}). \qquad \ldots.(3.9)$$

To obtain a complete set of equations we must add to the foregoing the relations governing the flow. Since the speed of flow, u, is much less than the speed of sound in the core, the fluid may be taken as incompressible. In this case, continuity of mass requires that

$$\nabla \cdot \boldsymbol{u} = 0 \qquad \ldots.(3.10)$$

and the equation of motion is

$$\rho \left(\frac{\partial \boldsymbol{u}}{\partial t} + (\boldsymbol{u} \cdot \nabla)\boldsymbol{u} \right) = -\nabla p + \rho \nabla V + \eta \nabla^2 \boldsymbol{u} + \frac{\mu}{4\pi} (\nabla \times \boldsymbol{H}) \times \boldsymbol{H}. \qquad \ldots.(3.11)$$

In the last equation p is the pressure, V is the gravitational potential and η the coefficient of viscosity ($\eta = \rho\nu$). The last term on the right hand side is no more than $\mu \boldsymbol{j} \times \boldsymbol{H}$, the electromagnetic ponderomotive force per unit volume which acts on the fluid.

Equation (3.9) should be compared with equation (3.3). It states that the magnetic field increases at a rate which is determined by the sum of two terms. The first represents the effect of resistance, and is always negative. The second expresses the inductive interaction between the motion and the field, and may, in some circumstances, be positive. Essentially, what BULLARD and ELSASSER have done is to seek steady solutions of equations (3.9) and (3.10) which give rise to an axial dipole field of the correct magnitude outside the core. In order to make any impression on the problem at all, it was necessary to assume $\boldsymbol{u}$. Due to great mathematical difficulties, the solution obtained was only approximate so that it cannot be asserted that there are definitely solutions of the required type. It has not been shown that $\boldsymbol{u}$ satisfies (3.11), a problem of even greater complexity than the first.

Let us try to gain an idea of how a conducting fluid in hydrodynamical motion interacts with a magnetic field. An observer of such a system would see not only motion of fluid particles, but also motion of the magnetic lines of force. (See Fig. 6.) We shall denote the velocity of an individual fluid particle by $\boldsymbol{v}$ and the velocity of the line of force at the position of the particle at the instant of observation by $\boldsymbol{c}$. Further, let the components of $\boldsymbol{v}$ and $\boldsymbol{c}$ perpendicular to the direction of $\boldsymbol{H}$ be $\boldsymbol{v}_\perp$ and $\boldsymbol{c}_\perp$. The law of motional induction states that the induced electromotive force is proportional to $\mu(\boldsymbol{v}_\perp - \boldsymbol{c}_\perp)H$ since motion parallel to the field cuts no line of force and hence gives rise to no induced e.m.f. LUNDQUIST (1952) has shown that

$$\boldsymbol{c}_\perp = \boldsymbol{v}_\perp + (\boldsymbol{j} \times \boldsymbol{H})/\sigma\mu H^2 \qquad \ldots.(3.12)$$

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It is readily seen from this equation that since $\boldsymbol{j}$ cannot be infinite, in an ideal conductor ($\sigma = \infty$), $\boldsymbol{v}_\perp = \boldsymbol{c}_\perp$, so that the lines of force move with the fluid. In the case of finite conductivity, the lines of force slip relative to the fluid by an amount $\boldsymbol{c}_\perp - \boldsymbol{v}_\perp$. If $(c_\perp - v_\perp)/v_\perp$ is much smaller than unity, the concept of an ideal conductor is fairly good. According to equations (3.12) and (3.5), this requires that

$$(LU\mu\sigma)^{-1} \ll 1 \qquad \ldots.(3.13)$$

if U is a velocity and L a length characteristic of the motion. This criterion is analogous to (3.4). In the case of the core (see Section 4) $(LU\mu\sigma)^{-1} = 10^{-2}$ so that the slipping of lines of force should not be great.

Let us now look at some of the features of the dynamo theory. LARMOR's

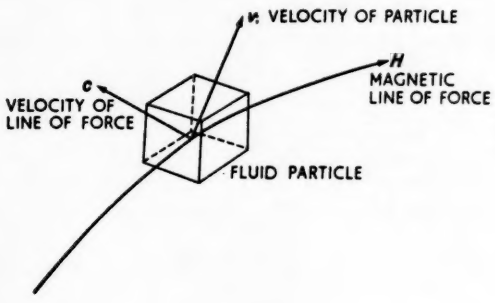

Fig. 6

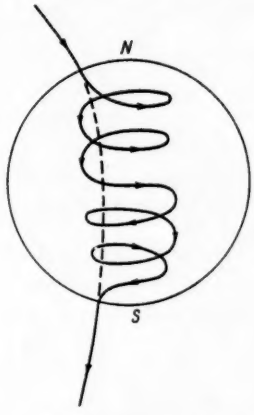

Fig. 7. Illustrating the production of a toroidal type of "contained" magnetic field by the action of zonal flow on a dipole field.

(1919) initial suggestion was that steady meridional circulation of matter (without a component parallel to latitude circles) could, through inductive interaction with a small inducing field parallel to the magnetic axis, produce zonal electric currents that amplify the inducing field. No explanation of the meridional circulation was given. LARMOR's simple mechanism will not work, as was shown by COWLING (1933) who demonstrated that steady motion confined to meridian planes is incapable of amplifying a field of the type required.

ELSASSER (1947) has proved another important theorem that entirely zonal motion parallel to latitude circles cannot amplify an inducing field of the required type (a dipole). The effect of such a motion is, in general, to stretch the lines of force within the core into a "toroidal" field in which the lines of force are pulled out zonally, (see Fig. 7). The field outside the fluid remains unchanged. The toroidal field would be a "contained" field (see above).

No one has been able to demonstrate conclusively that in more general circumstances the dynamo process could amplify a dipole field, but one thing is clear, namely, that the hydrodynamical flow involved must be more complicated

than the two extreme cases to which the theorems of COWLING and ELSASSER apply.

It was due to the apparent non-feasibility of a general approach that it was necessary to proceed in the manner already indicated, that is, to assume $\boldsymbol{u}$ in equation (3.9). ELSASSER developed an elegant mathematical formalism for treating this equation, which was extended and employed by BULLARD to construct a series of interactions which might suffice. An enormous amount of ingenuity was required, and in this connection, a recent paper by PARKER (to be published) deserves attention. The numerical calculations involved have been taken a great distance, and although we cannot be absolutely certain that the dynamo theory is correct, BULLARD (BULLARD and GELLMAN, 1954) concludes that ". . . the dynamo theory does provide a self-consistent account of the origin of the earth's magnetic field that raises no insuperable difficulties in other directions."

The Internal Magnetic Field of the Earth

One feature of both the thermoelectric and dynamo theories is the existence of contained fields within the earth. For example, as we shall see in Section 4, a toroidal field due to zonal fluid flow is an essential feature of BULLARD's theory, the strength of which he puts at about 50 gauss. The possibility of the existence of very strong magnetic fields within the earth (and stars for that matter) is important, since it would necessarily alter the entire perspective in which we view the comparatively feeble surface field; indeed, as someone has put it, "a mere whisp leaking out". If such strong fields exist, an important field of study would be the examination of all their geophysical consequences.

Clearly, it is important to seek methods by which the magnetic state of the earth's interior may be examined that do not depend on particular geomagnetic theories. RIKATAKE (1952) has concluded that in the core H does not exceed 10^4 gauss. His result is based on a calculation of the reflection coefficient of S waves at the core-mantle boundary. The idea embodied in his calculation is that since the reflection coefficient is high, not much energy can be carried off into the core by magneto-hydrodynamic waves (ALFVEN, 1950) from the point of incidence.

HIDE and RUNCORN (to be published) have examined the electro-magnetic damping of P waves within the earth. Since P waves are known to suffer little attenuation and the conductivity of the earth is such that very strong fields would cause appreciable damping, it can be shown that nowhere does H exceed 10^6 gauss.

Although by definition contained fields do not contribute to the magnetic field at the surface, they are associated with electric fields which would not vanish there. The electric field strength at the surface implied by BULLARD's toroidal magnetic field of 50 gauss is very small, although LOWES, following a suggestion by RUNCORN, hopes to investigate whether it exists.

Having attempted to give the main topic of this paper its perspective, we can summarize the foregoing remarks as follows: The earth's magnetic field is due to ordinary electric currents circulating within the earth. These currents are probably generated in some way by hydrodynamical motion of the liquid conducting core. Hence, a satisfactory theory of the earth's magnetism requires, in the first instance, a theory of core hydrodynamics.

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4. HYDRODYNAMICS OF THE CORE

Core hydrodynamics resolves itself into two major problems. First, we must discover the *cause* of hydrodynamical flow in the core, that is to say, we must find the ultimate source of energy from which the kinetic energy of fluid motion derives. This is equivalent to specifying the method by which a torque is continuously applied to the axle of the homopolar dynamo. The second major problem is that of elucidating in detail the dynamics, i.e. the behaviour in space and time, of the flow. The equivalent problem in the case of the homopolar dynamo is, of course, trivial; in the case of the core it is one of great complexity.

The Cause of Core Motions

In the case of the homopolar dynamo, the axle can only be maintained in a state of constant rotation provided that the applied torque can supply energy to the system at a rate equal to the sum of the rates at which mechanical friction and electrical resistance degrade kinetic and magnetic energy into heat. Knowing the rate of energy dissipation, we can say how potent the ultimate energy source must be. This is how we must examine the energetics of the core.

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The Magneto-hydrodynamic Energy Equation

To construct this equation we shall examine the magnetic energy balance within a volume of fluid, τ, fixed in space, the surface of which will be denoted by S. The volume and surface elements will be denoted by $\mathrm{d}\tau$ and $\mathrm{d}\boldsymbol{S}$. The full details of this calculation are given in an appendix, only the major steps will be indicated here.

On multiplying equation (3.8) scalarly by $\boldsymbol{j}/\sigma$ and integrating over the whole volume the result that

$$\frac{\partial M_i}{\partial t} + F_E = -J + N \qquad \ldots.(4.1)$$

is readily obtained, where

$$M_i \equiv \iiint_\tau \frac{\mu}{8\pi} H^2 \,\mathrm{d}\tau, \qquad \ldots.(4.2)$$

$$J \equiv \iiint_\tau (j^2/\sigma)\,\mathrm{d}\tau, \qquad \ldots.(4.3)$$

$$F_E \equiv \frac{1}{4\pi} \iint_S \boldsymbol{E} \times \boldsymbol{H} \,.\, \mathrm{d}\boldsymbol{S} \qquad \ldots.(4.4)$$

and

$$N \equiv \frac{\mu}{4\pi} \iiint_\tau \boldsymbol{u} \,.\, (\boldsymbol{H} \times (\nabla \times \boldsymbol{H}))\,\mathrm{d}\tau. \qquad \ldots.(4.5)$$

M_i is immediately recognized as the total magnetic energy within τ, and $M_i > 0$. F_E is the Poynting flux of electromagnetic energy leaving τ by the surface, S, so that if M_e is the magnetic energy outside τ and $(\partial M_e/\partial t)$ is the rate at which M_e is increasing due to processes occurring within τ,

$$F_E = \partial M_e/\partial t. \qquad \ldots.(4.6)$$

J is the rate at which magnetic energy is degraded by Joule heating and is essentially positive.

From our point of view, the most interesting term is N, the rate at which magneto-hydrodynamic forces transfer energy from the fluid motion to the magnetic field, since if $N = 0$ and $(\partial M_e/\partial t) > 0$, (the latter implying that the field energy within τ is not due to processes external to the volume) M_e decays with time.

We shall now evaluate N. This can be done by multiplying equation (3.11) by $\boldsymbol{u}$ and integrating over τ. Thus, it may be shown that

$$N = -(\partial K/\partial t) + F_K + F_p + F_\eta - D + G \qquad \ldots.(4.7)$$

where

$$K \equiv \frac{1}{2}\iiint_\tau \rho u^2 \, \mathrm{d}\tau, \qquad \ldots.(4.8)$$

$$F_K \equiv -\frac{1}{2}\iint_S \rho u^2 \boldsymbol{u} \,.\, \mathrm{d}\boldsymbol{S}, \qquad \ldots.(4.9)$$

$$F_p \equiv -\iint_S \rho \boldsymbol{u} \,.\, \mathrm{d}\boldsymbol{S}, \qquad \ldots.(4.10)$$

$$F_\eta \equiv \iint_S \eta(\boldsymbol{u} \times (\nabla \times \boldsymbol{u}) \,.\, \mathrm{d}\boldsymbol{S}, \qquad \ldots.(4.11)$$

$$D \equiv \iiint_\tau \eta \, |\nabla \times \boldsymbol{u}|^2 \, \mathrm{d}\tau, \qquad \ldots.(4.12)$$

and

$$G \equiv -\iiint_\tau \rho(\boldsymbol{u} \,.\, \nabla V) \, \mathrm{d}\tau. \qquad \ldots.(4.13)$$

The physical meaning of the terms defined by the foregoing equations is the following. K is the total kinetic energy. F_K is the flux of kinetic energy *into* the volume τ from any surrounding fluid, since we have included a negative sign in our definition. F_p is the flux of energy due to the action of normal pressure forces on the boundary S. F_η is the rate at which tangential mechanical forces transmit energy to τ through the agency of viscosity, due to velocity shear at S. D is the rate of viscous dissipation into heat and is always positive. Finally, G is the rate at which gravitational potential energy is released.

Since, as we shall see later, G is probably of great importance in the core, let us examine it rather more closely. Clearly, a necessary condition for G to be non-zero is that $\boldsymbol{u}$ has a component in the direction of gravity, ∇V, that is to say, $\boldsymbol{u}$ has a vertical component. Further, the sign of G depends on the correlation between the density field and the velocity field. G is positive or negative according to whether, on average, the rising fluid is less or more dense that the falling fluid. This is, of course, intuitively obvious.

G may be separated into two parts,

$$G = F_G + G_\tau, \qquad \ldots.(4.14)$$

where

$$F_G = -\iint_S \rho V \boldsymbol{u} \,.\, \mathrm{d}\boldsymbol{S} \qquad \ldots.(4.15)$$

and

$$G_\tau = \iiint_\tau V \boldsymbol{u} \,.\, \nabla\rho \, \mathrm{d}\tau. \qquad \ldots.(4.16)$$

F_G is the flux of gravitational energy into the volume τ such as we would find if a dense particle of fluid fell into τ, displacing a lighter particle. G_τ is the rate at which gravitation energy is released through any tendency for the fluid motion to redistribute the density field. Such a release of energy could be made continuous if the tendency for an initial density distribution to be altered by the fluid motion were offset by some external agency. An applied heat source might be this agency, the density changes being caused by thermal expansion.

On combining equations (4.1), (4.6), (4.7) and (4.14), we obtain the magnetohydrodynamic energy equation for a volume of incompressible fluid, expressing the rates at which the sum of the magnetic and kinetic energies increase with time in terms of the hydrodynamical properties of the flow, namely

$$(\partial/\partial t)(M_i + K) = -J - D + G_\tau + F \qquad \ldots.(4.17)$$

where F, the total flux of mechanical magnetic and gravitational energy into the system is just

$$F = F_K + F_p + F_\eta + F_G + F_E. \qquad \ldots.(4.18)$$

If the energy of the system is not changing with time

$$G_\tau + F = J + D, \qquad \ldots.(4.19)$$

that is to say, the energy supply must balance Joule heating and viscous dissipation into heat.

In order to apply this equation to the core, first we must estimate J and D before examining what possible contributions to the left hand side of equation (4.19) would enable us to satisfy the equation. This will tell us the likely cause of core motions. A clear-cut discussion of this problem is due to BULLARD (1949b), who will be followed here. His work will not be described in detail but some of his major arguments will be presented.

Energy Dissipation in the Core

The value of J may be estimated as follows: The total magnetic energy $M = M_e + M_i$, is 10^{28} ergs assuming the existence of a toroidal field of 50 gauss in the core (other fields being negligible in comparison). In the absence of an external agency to maintain the field, it would decay to e^{-1} of its initial value of $(4\sigma R_c^2/\pi) = 5 \cdot 10^{11}$ sec (see Section 3), hence $(\partial M/\partial t) \doteqdot 2 \cdot 10^{16}$ erg/sec and therefore $J \doteqdot 2 \cdot 10^{16}$ erg/sec.

Viscous dissipation measured by D can be roughly estimated if we introduce characteristic velocity and length parameters, U and L, and replace $(\nabla \times \boldsymbol{u})$ by U/L in equation (4.12). Employing the value of η given in Table I, and U and L equal to 10^{-1} cm/sec and 3×10^8 cm respectively (see below), D lies somewhere between 10^4 and 10^{16} erg/sec, the range reflecting the uncertainty in the coefficient of viscosity η. Since η is more likely to have the smaller than the larger value quoted in Section 2, $D \ll 10^{16}$ erg/sec and hence we can ignore D compared to J, most of the degradation of energy in the core being a consequence of Joule heating rather than viscosity.

Energy Generation in the Core

As we have just shown, whatever the major energy source in the core might be, it must be capable of delivering $2 \cdot 10^{16}$ erg/sec in the form of kinetic and magnetic energy.

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According to equation (4.19) there are two general energy "sources" corresponding to the terms G_τ and F. As we have seen, G_τ is the rate at which gravitational potential energy is released throughout the volume. F is the rate at which energy is transmitted from outside. For example, if we move in a coordinate system rotating at the mean rate of the earth, the mantle is accelerated relative to this system, due to causes we shall enumerate below. The effect on the core of such accelerations depends on many factors. Let us suppose that the mantle remains intact so that $F_K = F_G = 0$. Further, if the core is non-viscous ($F_\eta = 0$) and the mantle is rigid ($F_p = 0$) and no electric currents link the core and mantle ($F_E = 0$), $F = 0$. Thus, the core would not be coupled to the mantle and would move independently of it. However, if $G_\tau = 0$ also, there would be no energy source in the core, and the core would move as a whole, that is to say, no hydrodynamical motion would ensue.

If we relax one of the above conditions and let η be non-zero, the upper part of the core would be compelled to move with the mantle. This would give rise to velocity gradients and therefore a contribution F_η. This is what we mean when we say that energy may be communicated to a body of fluid through the agency of viscosity acting on velocity gradients at the boundary.

If, by some mechanism, the acceleration of the mantle generates electrical currents the possibility of coupling through the term F_E arises. BULLARD (1949b) has shown that electromagnetic coupling is much more effective than viscous coupling.

In case the mantle is not perfectly rigid and, for some reason or other, undergoes radial oscillations, normal pressure forces would transmit energy to the core. We choose our surface S to be just inside the core, with respect to which the core-mantle boundary oscillates radially, giving rise to a contribution F_p.

In Section 1 it was stated that virtually all naturally occurring fluid motions are due, ultimately, to the action of gravity. The gravitational potential in the proximity of the earth is the sum of two components, namely, that due to the earth itself, V_i and that due to extra-terrestrial sources (the moon and sun) V_e. Within the earth $|V_i| > |V_e|$, so that V_i would not be important in a term like G_τ (see equation 4.16). However, since the earth rotates, V_e varies with time with respect to an observer rotating with the earth, whereas, V_i does not. V_e gives rise to accelerations of the earth with respect to its mean motion, and may contribute to the energy balance in the core through F. Thus, a separate discussion of F and G corresponds roughly to a separate examination of the possible effects of V_e and V_i on core motions.

Gravitational Fields of Extra-Terrestrial Origin

It is well known that that mantle undergoes complicated accelerations, which are the following:

(1) The bodily tide.

(2) A gradual deceleration of the rate of rotation due to tidal friction in the oceans.

(3) Precession and nutation.

(4) Sudden changes in the rate of rotation.

Items (1) (2) and (3) are certainly due to V_e. The cause of item (4) is unknown. The influence of these accelerations on core motions was first discussed

several years ago, notably by ELSASSER and BULLARD. For the details of their arguments, the reader is referred to the original papers. Only the major results will be listed below.

The Bodily Tide of the Earth

It is well known that the mantle undergoes a radial tidal oscillation due to the earth's rotation in the proximity of the moon. JEFFREYS (see ELSASSER 1950b) has computed the amplitude of the oscillation at the core-mantle boundary, arriving at a value of 6 cm. The contribution to the energy of the core would be through F_p and ELSASSER (1950b) shows effectively that it would not amount to more than a minute fraction of J.

Tidal Friction

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The frictional forces accompanying tides in the ocean (which are, of course, due mainly to the moon) decelerate the rotation of the mantle. In general, we might expect that velocity gradients in the core and electric currents threading the core mantle boundary to be generated, giving rise to contributions through F_η and F_E. BULLARD (1949b) has examined this problem in some detail. He showed that the electromagnetic coupling between the mantle and core is so strong as to compel the core to follow the tidal deceleration of the mantle very closely, and less than $10^{-3}J$ ergs/sec could be transmitted to the core as kinetic and magnetic energy in this way.

Precession and Nutation

The precession of the mantle manifests itself as a motion of the rotation axis axis about a 24° cone with a period of 27,000 years. It is caused largely by the moon's inhomogeneous gravitational field acting on the obliquely orientated gravitational quadrupole of the earth. Nutation is a fluctuation of smaller amplitude and period superposed on precession. BULLARD (1949b) has discussed their influence on the core as follows: POINCARÉ (see LAMB, 1932) has shown that the ellipticity of the earth is large enough for even a non-viscous core to follow the precessing mantle as a rigid body in case the precessional amplitude is small. The coupling implied is entirely through the agency of normal pressure forces. However, we cannot be certain that POINCARÉ's theorem applies to the core since it has not been demonstrated to hold for finite amplitude, and the stability of the motion has not been discussed. Further examination of the problem proves inconclusive (BONDI and LYTTLETON, 1953), the mathematical difficulties being very considerable.

If the core fails to precess, very energetic fluid motions might be induced which would, on BULLARD's dynamo hypothesis, produce magnetic fields much stronger than these observed. On this count, BULLARD (1949b) tentatively suggests that POINCARÉ's theorem must be obeyed very closely. Clearly, this problem deserves further attention. It is interesting to note here that the apparent polarity reversals of the geomagnetic dipole (see Section 3) were associated with a time scale comparable with the precessional period.

BULLARD (1949b) also discards nutation as an insignificant influence on core motions.

Sudden Changes in the Rate of Rotation of the Mantle

It has been known for a long time that the earth's rotation rate occasionally changes quite suddenly by minute amounts, sometimes positive and sometimes negative (SPENCER-JONES, 1939). These changes are separated in time by intervals of several decades which BULLARD (1949b) has pointed out to be the only other geophysical phenomenon with the time scale of the secular variation. The cause of these changes is unknown.

BULLARD (1949b) showed that such accelerations of the mantle could not generate significant effects in the core. However, recent work by several authors (RUNCORN, 1954; MUNK and REVELLE, 1952; VESTINE, 1952) establishes the likelihood that sudden changes in the length of the day are a consequence and not the cause of core motions.

Because, with the possible exception of precession, the accelerations of the mantle cannot cause hydrodynamical flow in the core, let us examine the possible effects of the earth's own gravitational field.

The Effect of V_i on the Core

The earth's gravitational field may generate core motions if density inhomogeneities are present. There are two important types of flow that may be induced in this way, depending on the method by which $\nabla\rho$ is set up and maintained (see equation 4.14). One might be termed "sedimentation" and the other is thermal convection.

"*Sedimentation*"

If material were continuously falling out of the mantle into the core, fluid motions would ensue. The amount of energy thus delivered to the core each second would be $F_K + F_G$. The first of these terms F_K is due to the kinetic energy of the matter as it enters the core, which it has gained through falling in the mantle. F_G is the rate of gravitational energy release due to the displacement of fluid out of the core by the heavier material falling in. We expect such a process to be quite slow, so that $F_K \ll F_G$.

UREY (1952) has developed a theory of the earth's origin in which he suggests that the central condensation of the earth is still proceeding. He proposes that large local concentrations of iron are present in the mantle, which are slowly seeping through into the core. If this be so, $F_G = J = 2 \times 10^{16}$ erg/sec would not be unreasonable.

UREY goes on to propose that if this condensation process is fairly erratic, dense chunks of the mantle occasionally breaking off into the core, a fairly natural explanation of the sudden changes in the length of the day might follow. However, this proposal could only account for decreases in the length of the day since only decreases of the moment of inertia could be produced in this way.

Thermal Convection

If there are sources of heat in the core, thermal expansion will give rise to density inhomogeneities. The non-uniform density field would imply a contribution through G_τ.

The proposal that powerful thermally driven motions exist in the core was first made by ELSASSER (1939) and FRENKEL (1945) although BULLARD (1949) has given more cogent arguments than those given by these authors.

The total heat generated in the core is not known. In the absence of inhibition due to viscosity, thermal conduction, rotation and magnetic fields (see Section 1) convection would certainly occur if the heat supply exceeds that required to maintain the heat flow by conduction along the adiabatic gradient

$$H_a = 4\pi\chi\bar{R}^2(\mathrm{d}T/\mathrm{d}R)_a:$$

(where $\bar{R}$ is the mean radius of the core). This turns out to be 10^{11} cal/sec on inserting the data of Table I.

In a real fluid, the adiabatic gradient must be exceeded by an amount capable of maintaining convection against various damping influences. It follows from a theoretical result of CHANDRASEKHAR's (1954) (see also Section 1) that the depth of the core is so large that the amount by which the adiabatic gradient must be exceeded is negligible, so that if only slightly more than 10^{11} cal/sec are generated in the core, convection will certainly occur.

BULLARD (1949b) treats the mechanism whereby the thermal energy of the heat source is transformed into magnetic energy through the agency of fluid motion as a heat engine. If the temperature difference between the bottom and top of the convective region is $T_b - T_a$ and the temperature of the bottom is T_b, the theoretical thermodynamical efficiency $\varepsilon = (T_b - T_a)/T_b$ and on inserting typical values from Table I we find that $\varepsilon = 0{\cdot}1$. If the heat supply is 10 per cent more than that required to maintain the flow of 10^{11} cal/sec by conduction along the adiabatic gradient, then even if the mechanism has only one half of its theoretical thermodynamic efficiency, 2×10^{16} erg/sec would be available for conversion into magnetic energy, which is just the rate at which the latter would be depleted through Joule heating.

We may look at the problem in a slightly different way. We require that $G_\tau = 2 \times 10^{16}$ erg/sec. If $\bar{U}_R$ is a typical speed of radial flow and ΔT_ϕ is the temperature difference between rising and falling currents, at least to an order of magnitude, equation (4.16) leads to the result that

$$G_\tau \approx g\alpha\bar{R}^3(\bar{U}_R\Delta T_\phi), \qquad \ldots.(4.20)$$

and on inserting the values for g, α and $\bar{R}$ we find that

$$\bar{U}_R\Delta T_\phi = 2 \times 10^{-7}. \qquad \ldots.(4.21)$$

Most of the energy supply over and above that required to maintain the adiabatic gradient is transported bodily by the fluid. To an order of magnitude this convective heat transport H_c may be estimated by combining equations (3.1) and (4.21), yielding the result

$$H_c = 10^{10} \text{ cal/sec}. \qquad \ldots.(4.22)$$

This is somewhat less than the heat flow by conduction H_a.

Heat Sources in the Core

We have no knowledge of any heat sources in the core. The question arising from the preceding calculation is whether 10^{11} cal/sec is a reasonable rate of generation. The last figure corresponds to a mean rate of 3×10^{-17} cal/sec in each gram of core material. This is only 3×10^{-3} of the radioactive heating in acid igneous rocks, and BULLARD (1949b) on the grounds of this calculation, suggested that there may be minute concentrations of uranium and thorium in the core.

ELSASSER (1946b) proposed that the heavy oxides of thorium and uranium sank to the central body when the earth was formed, but UREY (1952) finds such a process difficult to accept.

If we do not assume a spherically symmetrical model, the conditions for convection appear to be more favourable, as was pointed out by BULLARD (1949b), and motions might ensue even if heat is generated at quite a small rate. This is due to the fact that fluid motion must arise if the surfaces of equal density and of equal gravitational potential do not coincide. They only coincide in a rotating liquid ellipsoid if the heat source distribution has a very special form which would not, in general, be expected to obtain. This is, effectively, a consequence of VON ZEIPEL's famous theorem (VERHOOGEN, 1948).

The Heat Balance of the Core

Since only a small fraction of the heat released would be converted into magnetic and kinetic energy, we must inquire as to its ultimate fate. The amount of heat to be disposed of is 10^{11} cal/sec. If we accept the values for the thermal conductivity of the mantle and the temperature gradient there given in Table I, heat flow by conduction in the mantle is about 10^{11} cal/sec, in which case there is no difficulty in getting rid of the heat from the core by conduction. However, as χ is not really known to any accuracy, we cannot definitely conclude that conduction will suffice. If convection occurs in the mantle (see Section 1), it would materially assist conduction.

If we assume that the core is thermally insulated by the mantle, all the heat would raise the temperature of the core as a whole. However, the total temperature rise in 4×10^9 years would only be a few tens of degrees Centigrade and would not be expected to produce any serious geophysical effects (ELSASSER, 1946b).

Having discussed the energetics of core motions, we can conclude that three possible major sources of energy might be available, namely, precession, UREY's sedimentation process and radioactive heating. A final decision between these three possibilities cannot be made at present.

Dynamics of Core Motions

While the studies of the cause of core motions have been fairly rewarding, the much more difficult problem of the dynamics is hardly understood at all. BULLARD (1949b), has, of course, devised a velocity field in connection with his dynamo hypothesis and in view of the success of his theory, we might describe in general terms the velocity field he invoked.

Bullard's Velocity Field and the Geomagnetic Westward Drift

Thermal convection must be associated with rising and falling motion, so that $\boldsymbol{u}$ has a radial component u_R. The form of this motion is assumed to be symmetrical about the earth's equatorial plane.

If, during their motion, individual fluid particles tend to conserve their angular momentum, the mixing due to the radial flow would produce an inward flux of angular momentum, giving rise to a variation with R of u_ϕ, the zonal component of flow, such that the outer part of the core rotates more slowly than the inner part. For such a velocity distribution to be steady, the bodily inward

flux of angular momentum must be exactly balanced by a frictional flux outward. BULLARD (1949b) showed that although viscosity would be inadequate to provide this frictional flux, it could easily be due to electromagnetic forces. Further, except at the outer extremity of the core, where viscosity demands that there be no motion relative to the mantle, the electromagnetic coupling between the core and mantle could allow the outer part of the core to move westward relative to the mantle. Secular variation sources, which are located in the outer part of the core, would therefore drift westward.

The magnitude of U_R and U_ϕ (capitals denoting orders of magnitude) emerges from BULLARD's dynamo theory (BULLARD and GELLMEN, 1954). Essentially, he reduced equations (3.9) and (3.10) to an eigenvalue problem, the eigenvalues giving the required U_ϕ and U_R for the rate at which hydromagnetic forces renew the field energy to balance the rate at which Joule heating degrades it into heat. It was found that U_ϕ is about 10^{-1} cm/sec and U_R about 10^{-3} cm/sec. This value of U_ϕ agrees with that of the geomagnetic westward drift, so that here we have a neat, attractive explanation of this phenomenon.

The main assumption upon which BULLARD's theory of the westward drift is based is that there is a tendency for individual fluid particles to conserve their angular momentum. The assumption, though *a priori* a very reasonable one, is not generally valid, as we shall see later. It might be mentioned here that the assumption applied to the earth's atmosphere fails to account for the winds there, except, perhaps, near the equator. Nor could it explain why the equatorial regions of the solar atmosphere rotate *faster* than the poles.

RUNCORN (1954) has proposed an alternative explanation of the westward drift. He interprets the small sudden changes in the length of the day as being due to torques applied to it when electromotive forces are suddenly generated at the core-mantle interface, perhaps thermo-electric electromotive forces generated when a hydrodynamical disturbance suddenly makes its presence felt at the core surface. These torques would not only act on the mantle, but would react on the core and may move it westward. There seems to be some quantitative evidence favouring this proposal.

The Dynamically Important Forces in the Core

It is interesting to try to estimate the order of magnitude of the terms in the hydrodynamical equation of motion. If $\boldsymbol{u}$ refers to the velocity relative to a system rotating at an angular velocity $\boldsymbol{\Omega}$, we must write

$$\rho\left[\frac{\partial \boldsymbol{u}}{\partial t} + (\boldsymbol{u}\,.\,\nabla)\boldsymbol{u} + 2\boldsymbol{\Omega}\times\boldsymbol{u} - \nu\nabla^2\boldsymbol{u}\right] - \frac{\mu}{4\pi}(\nabla\times\boldsymbol{H})\times\boldsymbol{H} = -\nabla\rho + \rho\nabla V \qquad \ldots.(4.23)$$

in place of equation (3.11), where $2\rho\boldsymbol{\Omega}\times\boldsymbol{u}$ is the so-called CORIOLIS force and the centrifugal force is absorbed in V. Equation (4.23) states that the sum of the forces due to dynamical accelerations, viscosity and electric currents balances the pressure forces (over and above the hydrostatic value) due to gravity acting on the density field.

Let us introduce a typical flow velocity U, a typical length scale, L, and magnetic field strength, H. If we replace ∇ by L^{-1} and $(\partial/\partial t)$ by U/L, on introducing these typical values in the left hand side of equation (4.23), we find that they may be written as in the following table:

Table III

Term in equation (4·23)	$\rho\frac{\partial \boldsymbol{u}}{\partial t}$	$\rho(\boldsymbol{u}\cdot\nabla)\boldsymbol{u}$	$\rho 2\boldsymbol{\Omega}\times\boldsymbol{u}$	$\rho\nu\nabla^2\boldsymbol{u}$	$\frac{\mu}{4\pi}(\nabla\times\boldsymbol{H})\times\boldsymbol{H}$.
Order of magnitude	$\rho U^2/L$	$\rho U^2/L$	$2\rho\Omega U$	$\rho\nu U/L^2$	$\mu H^2/4\pi L$.
Numerical value	3×10^{-10}	3×10^{-10}	10^{-4}	$10^{-20}-10^{-8}$	8×10^{-6}

For the want of a better estimate, we shall take $L = 3\times10^8$ cm, the size of a typical region secular variation of activity. H will be taken to be 50 gauss, the strength of BULLARD'S toroidal field. Ω is accurately known to be about 7×10^{-5} rad/sec. The kinematical viscosity coefficient ν is taken from Table I of Section 2.

The value to take for U is not too easy to estimate. The westward drift and other features of the geomagnetic field lead to $U = 0{\cdot}1$ cm/sec. It has been suggested by ELSASSER (1950a) that the systematic drift motion might be a good deal slower than the average speed involved, just as the general motion of weather patterns is slower than local wind speeds. He went further to suggest that there is equipartition between the average kinetic energy density, $\frac{1}{2}\rho U^2$, and the average magnetic energy density, $\mu H^2/8\pi$, which leads to $U = 5$ cm/sec. CHANDRASEKHAR (1950) and BATCHELOR (1950) have shown that only in the smallest eddies might equipartition be expected to exist. Secular variation periods much less than a few decades are not observed, presumably because of the screening effect of the conducting mantle, so that the fine structure of core motions is not revealed.

We have already seen that on BULLARD'S dynamo hypothesis $U_\phi = 10^{-1}$ cm/sec and $U_R = 10^{-3}$ cm/sec.

Let us take $U = 10^{-1}$ cm/sec, a value in which the uncertainty is hard to estimate. We are now in a position to compare the terms in equation (4.23), the numerical values of which are listed in Table III.

The next question is what can be concluded from these figures? We have seen an example in Section 1 of the type of argument we shall have to use here. Turbulence sets in a straight pipe when the inertial force, $\rho(\boldsymbol{u}\nabla)\boldsymbol{u}$ dominates the viscous force $\rho\nu\nabla^2\boldsymbol{u}$. The transition to turbulence from laminar motion arises when $(\rho U^2/L) \div (\rho\nu U/L^2) = UL/\nu = Re$, the Reynolds number, exceeds about 10^3, an empirical fact. Had experiments been lacking we might have put the critical Re at unity. Thus, it does not follow immediately that because one term in Table III is numerically greater than another, it is dynamically more influential.

We can be fairly certain that the inertial term $\rho U^2/L$ is less important than the Coriolis term, $2\rho\Omega U$. The ratio between these quantities, $(U/2L\Omega)$, is often called the Rossby number, and appears very frequently nowadays in the literature of dynamical meteorology. In the core $(U/2L\Omega) = 3\times10^{-6}$ and in the atmosphere, where the Rossby number is as high as 10^{-1} Coriolis forces certainly predominate over inertial forces.

In order to examine the relative importance of the Coriolis force and viscous force, we first note that since the Rossby number is small, the motion can be treated as slow and steady. This enables us to apply a result due to CHANDRASEKHAR (see Section 1) that when Ta (see equation 1.2), (which is no more than the

square of $(2\Omega\rho U) \div (\rho\nu U/L^2)$), exceeds 10^3, Coriolis forces are dynamically more important than viscous forces. We may safely conclude that this is so in the core where $10^8 \ll Ta < 10^{32}$.

According to Table III, there might be a temptation to suppose that Coriolis forces dominate electromagnetic forces. Perhaps a better way of comparing these two forces would be to make use of CHANDRASEKHAR's result (see Section 1) that when Ta is large, Coriolis forces are more or less influential than electromagnetic forces according as the quantity $(2\rho\Omega/\sigma H^2) \gtrless 1$. For the core, the last quantity is comparable with and perhaps slightly smaller than unity.

It would appear from the foregoing discussion that a first approximation to a dynamical theory of core motions might safely ignore viscous and inertial forces, but to omit either Coriolis forces or electromagnetic forces would lead to serious errors. To gain insight into the dynamics and magneto-hydrodynamics of rotating fluids, we shall conclude this article with some remarks on these topics.

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The Dynamics of Rotating Fluids

Let us introduce the valid approximation that inertial and viscous forces can be ignored in equation (4.23) and ignore, for the moment, the term containing $\boldsymbol{H}$. Thus, we shall write

$$\rho 2\boldsymbol{\Omega} \times \boldsymbol{u} = -\nabla p + \rho \nabla V. \qquad \ldots.(4.24)$$

Let us subtract from this equation the hydrostatic values of p and ρ by writing $p = p_0 + p_1$ and $\rho = \rho_0 + \rho_1$,

where
$$\rho_0 \nabla V = \nabla p_0, \qquad \ldots.(4.25)$$

so that if $\rho_1 \ll \rho_0$, which would be true in most cases of practical interest,

$$2\rho_0 \boldsymbol{\Omega} \times \boldsymbol{u} = -\nabla p_1 + \rho_1 \nabla V. \qquad \ldots.(4.26)$$

This is the so-called geostrophic equation which states that the dynamical pressure field due to gravity acting on the density field is entirely balanced by Coriolis forces. It is of great importance in dynamical meteorology.

If we take $\boldsymbol{\Omega}$ along the z-axis of Cartesian co-ordinates so that $\boldsymbol{\Omega} = (0, 0, \Omega)$, and operate on equation (4.26) with curl, the result that

$$2\Omega\rho_0 \frac{\partial \boldsymbol{u}}{\partial z} = \nabla\rho_1 \times \nabla V \qquad \ldots.(4.27)$$

is obtained. This equation leads to several important results.

The Proudman-Taylor Theorem

Many years ago, PROUDMAN and TAYLOR (TAYLOR 1921) discovered a theorem which states that "slow, steady relative motion of an inviscid flow of uniform density (and zero electrical conductivity), which otherwise rotates at a uniform rate, would be confined to planes perpendicular to the axis of rotation". The truth of this theorem, which is the basic one in the dynamics of rotating fluids, was demonstrated by an elegant experiment.

The theorem follows immediately from equation (4.27) if we write $\nabla\rho_1 = 0$ (uniform density), since then

$$\frac{\partial \boldsymbol{u}}{\partial z} = 0 \text{ and hence } \frac{\partial u_x}{\partial z} = \frac{\partial u_y}{\partial z} = \frac{\partial u_z}{\partial z} = 0, \qquad \ldots.(4.28)$$

where $\boldsymbol{u} = (u_x, u_y, u_z)$. In case u_z vanishes anywhere, as it must on a rigid boundary in the (x, y) plane, equation (4.28) implies that it vanishes everywhere which proves the theorem. The velocity component in the (x, y) plane $\boldsymbol{u}_H = (u_x, u_y)$ is independent of z, another important result.

We might pause here and consider the case of the core. One of the major requirements of a geomagnetic theory is an explanation of the near coincidence of the rotation and magnetic axes of the earth. This implies the existence of a certain asymmetry of the motions in the core, and it is readily seen that if the PROUDMAN-TAYLOR theorem holds there, we have a fairly natural explanation of the alignment of the geomagnetic dipole (BULLARD and GELLMAN, 1954; RUNCORN, 1954; ELSASSER, 1950a; FRENKEL, 1945). Unfortunately, the

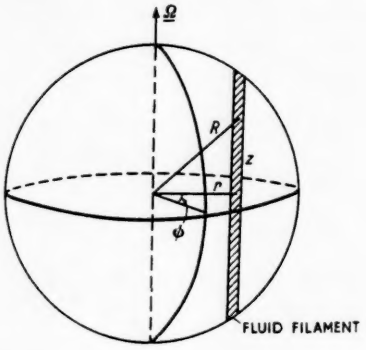

Fig. 8

theorem only holds exactly in the absence of significant electromagnetic forces, so that we cannot be certain whether it applies even approximately to the core.

Boundary Conditions

BULLARD and GELLMAN (1954) have shown that the two-dimensional theorem is even more restrictive in the case of a homogeneous fluid sphere surrounded by a rigid boundary (see Fig. 8). Clearly, a filament of fluid lying parallel to the z axis and terminating on the boundary can only move zonally, since any motion towards the rotation axis would involve a contraction of the filament in the z direction, that is u_z would not vanish and the theorem would be violated.

TAYLOR (1923a) has described some extraordinary phenomena arising when "three-dimensional" obstacles are towed in a rotating fluid.

The "Thermal Wind" Equation

Let us relax the condition that the fluid be homogeneous, and include the effects of $\nabla\rho_1$ in equation (4.24). It follows from this equation that the component of $\boldsymbol{u}$ along ∇V, $u_\parallel$ say, satisfies the equation

$$\frac{\partial u_\parallel}{\partial z} = 0 \qquad \ldots.(4.29)$$

and in the presence of boundaries upon which $u_\parallel$ vanishes, $u_\parallel$ must vanish everywhere. Thus, the flow would be confined to move along surfaces of equal gravitational potential, that is, horizontally. This is an approximate feature of

BULLARD's core motions, in which u_R is much smaller than u_ϕ. It is also a feature of the atmosphere, where the vertical motions are not easily detected by direct measurements. The confinement to horizontal surfaces is a less restrictive condition there that we have described above for a homogeneous fluid sphere.

Equation (4.27) expresses how the motion changes from one equipotential surface to the next in terms of the density field. It is well known in dynamical meteorology as the *thermal wind* equation, by which the meteorologist relates the vertical shear of horizontal winds to the horizontal temperature (density) field in the atmosphere.

Zonal Flow in a Gravitating Rotating Fluid Sphere

Let us consider a very simple case in which $\boldsymbol{u}$ has only an azimuthal component u_ϕ. According to equation (4.27)

$$2\rho_0 \Omega \frac{\partial u_\phi}{\partial z} = \frac{\partial V}{\partial r} \cdot \frac{\partial \rho_1}{\partial z} - \frac{\partial V}{\partial z} \cdot \frac{\partial \rho_1}{\partial r} \qquad \ldots.(4.29)$$

where (r, ϕ, z) are the usual cylindrical co-ordinates.

For the sake of argument, let us assume that the geomagnetic westward drift is due to a motion satisfying the last equation. We shall examine the general properties of the density field implied. Since the drift has the same sense in both hemispheres, u_ϕ is an even function of z and hence, $(\partial u_\phi/\partial z)$ is an odd function. Because $(\partial V/\partial z)$ is an odd function and $(\partial V/\partial r)$ is an even function of z, $\partial \rho_1/\partial z$ and $\partial \rho_1/\partial r$ must be odd and even functions respectively. This is, perhaps, the most reasonable assumption that could be made about the density field, since it implies symmetry about the rotation axis and the equatorial plane.

To an order of magnitude, if we introduce the temperature difference ΔT_R between the top and bottom of the core over and above the adiabatic value, and use the value of α given in Table I to relate the density and temperature, from equation (4.29) we find that

$$\bar{U}_\phi / \Delta T_R = 30, \qquad \ldots.(4.30)$$

and if $\bar{U}_\phi = 10^{-1}$ cm/sec, $\Delta T_R = 3 \times 10^{-3}$°C.

To obtain his particular distribution of u_ϕ, BULLARD (see above) assumed that individual fluid particles tend to conserve their angular momentum. The heat source distribution (which determines ρ_1) implied by BULLARD's u_ϕ when inserted in equation (4.29) is a very special one and we have no idea whether it would obtain in the core. Since we do not know how closely equation (4.29) applies to the core, the last remark cannot be taken as a serious objection to BULLARD's theory of the westward drift; the present discussion is intended to be only illustrative rather than illuminating.

Some Remarks on Magneto-hydrodynamics

We have already shown that magnetic fields are likely to be as influential dynamically as is rotation in the core. Since the magnetic field in the core has not the simple properties of $\boldsymbol{\Omega}$, we cannot examine its influence in a very satisfactory manner. However, a few comments will be made here because they do not appear to have been made in the literature of magneto-hydrodynamics, in which connection the reader is referred to the latest review of this subject (LUNDQUIST, 1952).

Let us consider the following simple problem: what are the properties of slow steady relative motions in an electrically conducting inviscid, inhomogeneous fluid, which rotates at a uniform rate, in the presence of a uniform magnetic field, $\boldsymbol{H}_0$, in a case where $\boldsymbol{\Omega}$ and $\boldsymbol{H}_0$ are parallel vectors?

Due to electromagnetic induction, the motion will give rise to electric currents which in their turn produce a magnetic field $\boldsymbol{h}$ (say). Since the motion is assumed to be slow, $h \ll H_0$. To a first approximation, the equations of our problem (equations (3.9) and (4.23)) may be written

$$\nabla^2 \boldsymbol{h} = 4\pi\sigma\mu H_0 \frac{\partial \boldsymbol{u}}{\partial z} \qquad \ldots.(4.31)$$

and

$$2\rho_0 \boldsymbol{\Omega} \times \boldsymbol{u} = -\nabla p_1 + \rho_1 \nabla V + \frac{\mu}{4\pi}(\nabla \times \boldsymbol{h}) \times \boldsymbol{H}_0, \qquad \ldots.(4.32)$$

since $\boldsymbol{H}_0 = (0, 0, H_0)$ and H_0 is constant. If we operate on the last equation twice with curl and introduce the vorticity

$$\boldsymbol{\omega} = \nabla \times \boldsymbol{u}, \qquad \ldots.(4.33)$$

we find that

$$\sigma\mu^2 H_0^2 \frac{\partial^2 \boldsymbol{u}}{\partial z^2} + 2\rho_0 \Omega \frac{\partial \boldsymbol{\omega}}{\partial z} = \nabla \times (\nabla\rho_1 \times \nabla V). \qquad \ldots.(4.34)$$

When, $\Omega = \nabla\rho_1 = 0$ and σ and H_0 do not vanish the last equation leads to the simple result that

$$\frac{\partial^2 \boldsymbol{u}}{\partial z^2} = 0, \quad \text{therefore } \frac{\partial^2 u_x}{\partial z^2} = \frac{\partial^2 u_y}{\partial z^2} = \frac{\partial^2 u_z}{\partial z^2} = 0. \qquad \ldots.(4.35)$$

It follows therefore that

$$u_z = f(x, y)z + g(x, y). \qquad \ldots.(4.36)$$

If u_z and $(\partial u_z/\partial z)$ vanish anywhere, then u_z must vanish everywhere, and we have a result in magneto-hydrodynamics analogous to the PROUDMAN-TAYLOR theorem in the dynamics of a rotating fluid. We do not know whether the foregoing result is of much interest, since no experiment to test it has been performed. It may be, for example, that steady flow cannot be produced under these conditions.

Deviations from Geostrophism

When $\Omega \neq 0$ but ρ_1 is constant, equation (4.34) could be satisfied by $u_z = 0$ and $\boldsymbol{u}_H = (u_x, u_y)$ independent of z. Further, since the flow is steady, by equation (3.6) $\nabla \times \boldsymbol{E} = 0$. If $\boldsymbol{E}$ vanishes, then equations (3.9) and (4.23) lead to the result that

$$2\rho_0 \boldsymbol{\Omega} \times \boldsymbol{u}_H = -\nabla_H p_1 - \sigma\mu^2 H_0^2 \boldsymbol{u}_H, \qquad \ldots.(4.37)$$

where the subscript H denotes that we are dealing with the (x, y) components only, which are given by

$$\left.\begin{aligned} -2\rho_0 \Omega u_y &= -\frac{\partial p_1}{\partial x} - \sigma H_0^2 \mu^2 u_x, \\ +2\rho_0 \Omega u_x &= -\frac{\partial p_1}{\partial y} - \sigma H_0^2 \mu^2 u_y. \end{aligned}\right\} \qquad \ldots.(4.38)$$

Multiply the first of these equations by $i = \sqrt{-1}$ and add it to the second, to obtain the result that

$$(\sigma\mu^2 H_0^2 + 2\rho_0\Omega i)(u_x + iu_y) = -\left(\frac{\partial p_1}{\partial x} + i\frac{\partial p_1}{\partial y}\right). \quad \ldots.(4.39)$$

If we introduce the "geostrophic wind" given by

$$2\Omega\rho_0 i W_G = -\left(\frac{\partial p_1}{\partial x} + i\frac{\partial p_1}{\partial y}\right) \quad \ldots.(4.40)$$

and write

$$W = u_x + iu_y, \quad \ldots.(4.41)$$

then equation (4.39) becomes

$$W = W_G/(1 - i\sigma\mu^2 H_0^2/2\Omega\rho_0). \quad \ldots.(4.42)$$

W_G is everywhere directed along the isobars, according to its definition, and the actual motion always has this property if the pressure field is exactly balanced by Coriolis forces. When other forces are present, the fluid spills over the isobars and we then have "deviations from geostrophism". The angle between W and W_G namely, $\tan^{-1}(\sigma\mu^2 H_0^2/2\Omega\rho_0)$ measures this deviation, and it will be recalled that the tangent of this angle is the quantity that CHANDRASEKHAR (1954) found to determine the relative importance of rotation and a magnetic field in the case of inhibition of thermal convection in a fluid of small viscosity (see Section 1).

The "Thermal Wind Equation" When a Magnetic Field is Present

It is interesting to see how equation (4.26) is modified by the presence of a magnetic field. In the particularly simple case in which $\boldsymbol{\Omega}$, $\boldsymbol{H}_0$ and ∇V are parallel vectors and $\nabla V = (0, 0, -g)$ equation (4.34) has the three components

$$\left.\begin{aligned}
\sigma\mu^2 H_0^2 \frac{\partial^2 u_x}{\partial z^2} + 2\rho_0\Omega\frac{\partial \omega_x}{\partial z} &= -g\frac{\partial^2 \rho_1}{\partial z \partial x},\\
\sigma\mu^2 H_0^2 \frac{\partial^2 u_y}{\partial z^2} + 2\rho_0\Omega\frac{\partial \omega_y}{\partial z} &= -g\frac{\partial^2 \rho_1}{\partial z \partial y},\\
\sigma\mu^2 H_0^2 \frac{\partial^2 u_z}{\partial z^2} + 2\rho_0\Omega\frac{\partial \omega_z}{\partial z} &= g\left(\frac{\partial^2 \rho_1}{\partial x^2} + \frac{\partial^2 \rho_1}{\partial y^2}\right).
\end{aligned}\right\} \quad \ldots.(4.43)$$

From the last equation we can see that the near analogy between the effects of rotation ($H_0 = 0$) and a magnetic field ($\Omega = 0$) when ρ_1 is constant breaks down when density inhomogeneities are allowed. For if ρ_1 only depends on x and y, and $\Omega = 0$ equation (4.43) could be satisfied by $u_x = u_y = 0, u_z \neq 0$, whereas when $H_0 = 0$, we have already seen that the motion would be confined to horizontal surfaces, implying here that $u_x \neq 0$, $u_y \neq 0$, $u_z = 0$ since ∇V only has a z component.

APPENDIX

THE MAGNETO-HYDRODYNAMIC ENERGY EQUATION FOR AN INCOMPRESSIBLE FLUID

THE presence of a magnetic field in an electrically conducting fluid which is in hydrodynamical motion results, in general, in electrical currents impelled by the induced electromotive forces. These currents are associated with electromagnetic

ponderomotive forces which accelerate the fluid motion. They also modify the original magnetic field. The net result is an interchange between the energy of mass motion and the energy of the magnetic field. We shall examine the energy balance in such a system in case the fluid is incompressible. The derivation of the magneto-hydrodynamic energy equation presented below is equivalent to one given by Professor CHANDRASEKHAR in one of his seminars, and is reproduced by his kind permission.

The Equations of the Problem

We shall denote the magnetic and electric fields by $\boldsymbol{H}$ and $\boldsymbol{E}$ respectively and the electric current density by $\boldsymbol{j}$. The coefficients of magnetic permeability μ, and electrical conductivity, σ, will be assumed to be constant. We shall restrict attention to circumstances in which the velocities involved are much smaller than that of light so that displacement currents may be safely ignored. Electromagnetic units will be employed throughout.

MAXWELL's equations for our problem are as follows:

$$\nabla \times \boldsymbol{H} = 4\pi \boldsymbol{j}, \qquad \ldots.(A.1)$$

$$\nabla \times \boldsymbol{E} = -\mu \frac{\partial \boldsymbol{H}}{\partial t}, \qquad \ldots.(A.2)$$

and

$$\nabla \cdot \boldsymbol{H} = 0. \qquad \ldots.(A.3)$$

Since we are dealing with a fluid in motion, the electromotive forces which give rise to $\boldsymbol{j}$ are due both to electric charges and to motional induction. If the velocity of fluid flow at a point in space is $\boldsymbol{u}$, then we must write

$$\boldsymbol{j} = \sigma[\boldsymbol{E} + \mu \boldsymbol{u} \times \boldsymbol{H}]. \qquad \ldots.(A.4)$$

In the last equation, Hall currents are ignored.

A complete set of equations require that we add to the foregoing those governing the fluid flow. Since we are assuming that the fluid is incompressible, continuity of matter is expressed by the equation

$$\rho \nabla \cdot \boldsymbol{u} = 0 = -\left(\frac{\partial \rho}{\partial t} + \boldsymbol{u} \cdot \nabla \rho\right). \qquad \ldots.(A.5)$$

The equation of motion is the following:

$$\rho\left(\frac{\partial \boldsymbol{u}}{\partial t} + (\boldsymbol{u} \cdot \nabla)\boldsymbol{u}\right) = -\nabla p + \rho \nabla V + \eta \nabla^2 \boldsymbol{u} + \mu \boldsymbol{j} \times \boldsymbol{H}, \qquad \ldots.(A.6)$$

where ρ is the density, p the pressure, V the gravitational potential and η the coefficient of viscosity. The last term on the right hand side of this equation is the force per unit volume due to the electric currents. We have ignored the force due to the electric field acting on any charges that are present; this can be shown to be a valid procedure when u is much less than the speed of light.

Multiply equation (A.4) scalarly by $\boldsymbol{j}/\sigma$ and substitute for $\boldsymbol{j}$ on the right hand side from equation (A.1). Thus we find that

$$\frac{j^2}{\sigma} = \frac{1}{4\pi}\{\boldsymbol{E} \cdot \nabla \times \boldsymbol{H} + \mu(\boldsymbol{u} \times \boldsymbol{H}) \cdot \nabla \times \boldsymbol{H}\}. \qquad \ldots.(A.7)$$

By a well-known vector identity,

$$\nabla . (\boldsymbol{E} \times \boldsymbol{H}) = \boldsymbol{H} . \nabla \times \boldsymbol{E} - \boldsymbol{E} . \nabla \times \boldsymbol{H}, \qquad \ldots.(A.8)$$

so that on combining the last two equations with equation (A.2) we are led to the result that

$$\frac{\mu}{8\pi} \frac{\partial H^2}{\partial t} = -\frac{j^2}{\sigma} - \frac{1}{4\pi} \nabla . (\boldsymbol{E} \times \boldsymbol{H}) + \frac{\mu}{4\pi} (\boldsymbol{u} \times \boldsymbol{H}) . \nabla \times \boldsymbol{H}. \qquad \ldots.(A.9)$$

Consider a region within the fluid τ bounded by the surface S, and let the volume element be denoted by $d\tau$ and the surface element by the vector $d\boldsymbol{S}$ directed along the outward drawn normal. On integrating equation (A.9) over τ and employing Gauss' theorem to reduce the second term on the right hand side to a surface integral, we find that

$$\frac{\partial}{\partial t} \iiint_\tau \frac{\mu H^2}{8\pi} d\tau = -\iiint_\tau \frac{j^2}{\sigma} d\tau - \iint_S \frac{\boldsymbol{E} \times \boldsymbol{H}}{4\pi} . d\boldsymbol{S} + \iiint_\tau \frac{\mu}{4\pi} (\boldsymbol{u} \times \boldsymbol{H}) . \nabla \times \boldsymbol{H} \, d\tau. \qquad \ldots.(A.10)$$

The last equation states that the rate at which the magnetic energy is changing with time is the sum of the (negative) Joule heating, the Poynting flux of electromagnetic energy at the boundary, and the rate at which magnetic energy is derived from the kinetic energy of fluid flow. It is the main purpose of the following calculation to evaluate the last term.

First we note that since

$$\boldsymbol{a}.(\boldsymbol{b} \times \boldsymbol{c}) = \boldsymbol{b} . (\boldsymbol{c} \times \boldsymbol{a}) = \boldsymbol{c} . (\boldsymbol{a} \times \boldsymbol{b}), \qquad \ldots.(A.11)$$

$$(\boldsymbol{u} \times \boldsymbol{H}) . \nabla \times \boldsymbol{H} = \boldsymbol{u} . [\boldsymbol{H} \times (\nabla \times \boldsymbol{H})]. \qquad \ldots.(A.12)$$

Now substitute for $\boldsymbol{j}$ in equation (A.6) from (A.1) and rearrange, thus obtaining the equation

$$\frac{\mu}{4\pi} (\boldsymbol{H} \times (\nabla \times \boldsymbol{H})) = -\rho \left\{ \frac{\partial \boldsymbol{u}}{\partial t} + (\boldsymbol{u} . \nabla) \boldsymbol{u} - \nabla V \right\} + \eta \nabla^2 \boldsymbol{u} - \nabla p. \qquad \ldots.(A.13)$$

On multiplying the last equation scalarly by $\boldsymbol{u}$, integrating over τ, and making use of equations (A.10) and (A.12), the result that

$$\frac{\partial}{\partial t} \iiint_\tau \frac{\mu H^2}{8\pi} d\tau + \iiint_\tau \frac{j^2}{\sigma} d\tau + \iint_S \frac{\boldsymbol{E} \times \boldsymbol{H}}{4\pi} . d\boldsymbol{S} = -\iiint_\tau \left(\rho \boldsymbol{u} . \frac{\partial \boldsymbol{u}}{\partial t} + \rho \boldsymbol{u} (\boldsymbol{u} . \nabla) \boldsymbol{u} \right) d\tau + \iiint_\tau \rho \boldsymbol{u} . \nabla V \, d\tau + \iiint_\tau \eta \boldsymbol{u} . \nabla^2 \boldsymbol{u} \, d\tau - \iiint_\tau \boldsymbol{u} . \nabla p \, d\tau \qquad \ldots.(A.14)$$

is obtained.

We shall consider the terms on the right-hand side of the last equation separately.

Clearly,

$$\rho \boldsymbol{u} \cdot \frac{\partial \boldsymbol{u}}{\partial t} = \frac{1}{2} \frac{\partial (\rho u^2)}{\partial t} - \frac{1}{2} u^2 \frac{\partial \rho}{\partial t}. \quad \ldots.(A.15)$$

By the vector identity

$$\nabla(\boldsymbol{a} \cdot \boldsymbol{b}) = (\boldsymbol{a} \cdot \nabla)\boldsymbol{b} + (\boldsymbol{b} \cdot \nabla)\boldsymbol{a} + \boldsymbol{a} \times (\nabla \times \boldsymbol{b}) + \boldsymbol{b} \times (\nabla \times \boldsymbol{a}), \quad \ldots.(A.16)$$

$$(\boldsymbol{u} \cdot \nabla)\boldsymbol{u} = \tfrac{1}{2}\nabla u^2 - \boldsymbol{u} \times (\nabla \times \boldsymbol{u}), \quad \ldots.(A.17)$$

so that

$$\rho \boldsymbol{u} \cdot (\boldsymbol{u} \cdot \nabla)\boldsymbol{u} = \tfrac{1}{2}\rho \boldsymbol{u} \cdot \nabla u^2. \quad \ldots.(A.18)$$

Now make use of the identity

$$\nabla \cdot (a\boldsymbol{b}) = a\nabla \cdot \boldsymbol{b} + \boldsymbol{b} \cdot \nabla a \quad \ldots.(A.19)$$

and equation (A.5) to obtain the equation

$$\boldsymbol{u} \cdot \nabla u^2 = \nabla \cdot (\rho u^2 \boldsymbol{u}) - u^2 \boldsymbol{u} \cdot \nabla \rho = \nabla \cdot (\rho u^2 \boldsymbol{u}) + u^2 \frac{\partial \rho}{\partial t}. \quad \ldots.(A.20)$$

On combining equations (A.15, 18, 20) we find that

$$\rho \boldsymbol{u} \cdot \frac{\partial \boldsymbol{u}}{\partial t} + \rho \boldsymbol{u} \cdot (\boldsymbol{u} \cdot \nabla)\boldsymbol{u} = \tfrac{1}{2} \frac{\partial}{\partial t}(\rho u^2) + \tfrac{1}{2}\nabla \cdot (\rho u^2 \boldsymbol{u}). \quad \ldots.(A.21)$$

The integrand of the second term on the right-hand side of equation (A.14) may be written

$$\rho \boldsymbol{u} \cdot \nabla V = \nabla \cdot (\rho V \boldsymbol{u}) - V \boldsymbol{u} \cdot \nabla \rho \quad \ldots.(A.22)$$

in view of equations (A.5) and (A.19).

The integrand of the viscous term in equation (A.14) may be reduced as follows: First we note that

$$\nabla \cdot (\boldsymbol{a} \times \boldsymbol{b}) = \boldsymbol{b} \cdot \nabla \times \boldsymbol{a} - \boldsymbol{a} \cdot \nabla \times \boldsymbol{b} \quad \ldots.(A.23)$$

and

$$\nabla \times (\nabla \times \boldsymbol{a}) = \nabla \cdot (\nabla \boldsymbol{a}) - \nabla^2 \boldsymbol{a}. \quad \ldots.(A.24)$$

On combining these identities with equation (A.5), it is found that

$$\boldsymbol{u} \cdot \nabla^2 \boldsymbol{u} = \nabla \cdot (\boldsymbol{u} \times (\nabla \times \boldsymbol{u})) - |\nabla \times \boldsymbol{u}|^2. \quad \ldots.(A.25)$$

The integrand of the term containing the pressure

$$\boldsymbol{u} \cdot \nabla p = \nabla \cdot (\boldsymbol{u} p) \quad \ldots.(A.26)$$

in view of the continuity equation (A.5).

Finally, we can combine equations (A.21, 22, 25, 26) with equation (A.14) to obtain, after making further use of Gauss' theorem, the result that

$$\begin{aligned}\frac{\partial}{\partial t}\iiint_\tau \left(\mu \frac{H^2}{8\pi} + \frac{1}{2}\rho u^2\right) \mathrm{d}\tau &= -\iiint_\tau \frac{j^2}{\sigma}\,\mathrm{d}\tau \\ &- \iiint_\tau \eta |\nabla \times \boldsymbol{u}|^2 \,\mathrm{d}\tau - \iint_S \tfrac{1}{2}\rho u^2 \boldsymbol{u} \cdot \mathrm{d}\boldsymbol{S} + \iint_S \rho V \boldsymbol{u} \cdot \mathrm{d}\boldsymbol{S} \\ &- \iint_S \frac{(\boldsymbol{E} \times \boldsymbol{H})}{4\pi} \cdot \mathrm{d}\boldsymbol{S} - \iint_S p\boldsymbol{u} \cdot \mathrm{d}\boldsymbol{S} + \iint_S \eta(\boldsymbol{u} \times (\nabla \times \boldsymbol{u})) \cdot \mathrm{d}\boldsymbol{S} \\ &- \iiint_\tau V \boldsymbol{u} \cdot \nabla \rho \,\mathrm{d}\tau. \quad \ldots.(A.27)\end{aligned}$$

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This is the magneto-hydrodynamic energy equation for an incompressible fluid. To understand the physical meaning of this equation, we might discuss each term separately.

(1) $\frac{\partial}{\partial t}\int\int\int_\tau \frac{\mu}{8\pi} H^2 \, d\tau$ — is the rate of change of the total magnetic energy contained within τ.

(2) $\frac{\partial}{\partial t}\int\int\int_\tau \frac{1}{2}\rho u^2 \, d\tau$ — is the rate of change of the kinetic energy.

(3) $\int\int\int_\tau \frac{j^2}{\sigma} \, d\tau$ — is the rate at which Ohmic heating degrades the magnetic and kinetic energy into heat, since the integral is essentially positive.

(4) $\int\int\int_\tau \eta |\nabla \times \boldsymbol{u}|^2 \, d\tau$ — is the rate at which viscosity degrades the energy into heat.

(5) $-\int\int_S \frac{1}{2}\rho u^2 \boldsymbol{u} \, . \, d\boldsymbol{S}$ — is the net flux of kinetic energy into τ through S. This term may be positive or negative.

(6) $-\int\int_S \rho V \boldsymbol{u} \, . \, d\boldsymbol{S}$ — is the inward flux of gravitational energy. This term can take either sign.

(7) $-\int\int_S \frac{\boldsymbol{E} \times \boldsymbol{H}}{4\pi} \, . \, d\boldsymbol{S}$ — is the Poynting flux of electromagnetic energy into τ, which may be positive or negative.

(8) $-\int\int_S p\boldsymbol{u} \, . \, d\boldsymbol{S}$ — is the rate at which normal pressure forces acting at S tend to increase the energy within τ. In case this term is negative, then work is done by the fluid within τ on the surrounding medium.

(9) $\int\int_S \eta(\boldsymbol{u} \times (\nabla \times \boldsymbol{u})) \, . \, d\boldsymbol{S}$ — is the flux of energy due to the action of tangential viscous stresses at S. This quantity may have either sign.

(10) $\int\int\int_\tau V\boldsymbol{u} \, . \, \nabla\rho \, d\tau$ — is the rate at which gravitational potential energy is released by any tendency for the fluid motion to redistribute the density field, and may be positive or negative.

In case the boundary S is rigid, $\boldsymbol{u}$ must vanish on it. The terms (5), (6) and (8) would then vanish and the tangential viscous forces at S would do work on the boundary at a rate measured by term (9).

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INVESTIGATIONS UNDER HYDROTHERMAL CONDITIONS

By RUSTUM ROY and O. F. TUTTLE

INTRODUCTION

IT has long been known that volatile materials have played an important role in the genesis of the igneous and metamorphic rocks and it is perhaps the realization that this role is only partially understood which has stimulated many students of the earth's crust to undertake laboratory studies in hydrothermal* systems. Thus most of the contributions to our knowledge of systems involving volatile materials comes from laboratories which are primarily devoted to studies of problems in the Earth Sciences. It is obvious that if in nature minerals and mineral assemblages were formed at elevated temperatures and high pressures in the presence of volatile materials—chiefly water—it will be quite impossible to obtain any accurate reproduction of natural conditions or processes except under "hydrothermal conditions". Most of the early interest in this field stemmed from the desire to synthesize particular minerals, rather than from any attempt to obtain systematic data on the geochemistry of the earth's crust. Thus the studies to be reported here can in general be divided into three categories, 1. Mineral synthesis, 2. Subsolidus phase equilibrium investigations, and 3. Liquidus studies.

Progress in this branch of geochemistry depends to a large extent on the development of facilities for reproducing those extreme conditions of which nature has made use in producing and modifying the earth's crust. The remarkable post-war progress in hydrothermal research is due to a large extent to such a widening of facilities which in turn has come about in part as a result of the war-time development of new corrosion resistant alloys with high strength at elevated temperatures, and in part by new designs. As instrumentation is of such vital importance to hydrothermal studies, one section of this chapter will be devoted to a description of the various types of apparatus successfully used in systematic high pressure investigations.

The present survey of the literature is not intended to be comprehensive or exhaustive and we have been forced to omit reference to many papers which would have been included had unlimited space been available. Our survey of the literature aims at being critical and evaluatory to some extent and covering mainly the more recent and more quantitative work. Much of this recent work has been built on extensive earlier work which may not be mentioned herein though the latter is fully acknowledged and referenced in the original papers.

For more exhaustive surveys of the literature the reader is referred to the paper

* The term "hydrothermal" will herein be used in a broad sense and will include studies in which water is not a component such as in systems containing carbon dioxide. Also, the volatile material may be present as a liquid, as a vapour, dissolved in a silicate melt, or as a component of a crystalline phase.

by MOREY and INGERSON (1937) and a more recent survey, appearing during the course of preparation of this review, by EITEL (1954).

HISTORICAL REVIEW

The early studies on hydrothermal systems at elevated temperatures and pressures have been reviewed in detail by MOREY and NIGGLI (1913) and as no systematic quantitative studies were carried out before 1913 the reader is referred to their paper for a description of these early studies. MOREY and NIGGLI conclude, "In this paper we have assembled all of the available data relating to hydrothermal syntheses, data which unfortunately afford us practically no reliable quantitative information. Moreover, qualitatively even, the data leave much to be desired; for many minerals have been obtained but once by a given investigator, in a manner which was not reproducible and under conditions which were not specified".

Systematic studies of hydrothermal systems began with the publication of a pioneering study entitled, "The Ternary System H_2O—K_2SiO_3—SiO_2", by MOREY and FENNER (1917). Here, for the first time, studies were carried out in a systematic fashion with the temperature carefully controlled and measured and the pressure held constant throughout the experiment. The charges were prepared from pure materials and consequently the composition of the charges used in each experiment was precisely known.

This first study has important applications to geological processes because it was demonstrated that there is complete solubility between anhydrous compositions rich in silica, and water. Thus a mechanism for forming pegmatites by concentrating volatile materials during crystallization was demonstrated. It was also shown that the pressure on such a system which is gradually concentrating volatile materials during cooling may increase to a maximum at some temperature below the melting temperature of the anhydrous phases. This relationship is now accepted—by many petrologists—as a mechanism for inducing violent volcanic activity or the successive mild outbursts characteristic of many volcanic areas (see MOREY, 1922).

The next milestone in the study of hydrothermal systems was made possible by the design of a successful internally heated pressure vessel (SMYTH and ADAMS, 1923). Heretofore studies were limited to relatively low temperatures and pressures because the externally heated vessels failed as a result of creep and oxidation of the alloys used. The internally heated pressure vessel designed by ADAMS was cooled externally by circulating water, and pressures up to the cold strength of the alloys could theoretically be used at temperatures nearly as high as the melting temperatures of the windings used (i.e. platinum).

The first hydrothermal study using this equipment was carried out by GORANSON (1931). This investigation represents one of the most outstanding advances in the application of hydrothermal laboratory studies to petrological problems so far published. It was demonstrated that the solubility of water in a liquid having the composition of the Stone Mountain Granite was limited to a relatively small amount (i.e. < 10 per cent by weight) at pressures expected in the outer 20 km of the earth's crust. Also, from GORANSON's results it follows that the pressures generated in a crystallizing hydrous magma can be expected to reach values high enough to lift an overburden equivalent to at least 15 to 20 km of

rocks. Thus driving forces for volcanic activity were tied to crystallization of hydrous silicate liquids. This pioneering study by GORANSON was followed by studies on the binary systems $NaAlSi_3O_8$—H_2O and $KAlSi_3O_8$—H_2O in which he was able to present liquidus data in addition to the solubility of water in the melts.

The hydrothermal studies up to World War II include extensive literature on syntheses of various minerals but only the above mentioned can be considered as quantitative systematic studies of equilibrium relations. Rapid progress in this field was impossible because of the limits on pressure and temperature imposed by the externally heated pressure vessels and by the extremely complicated nature of the internally heated units. During and after the war the great interest in certain crystalline phases, especially quartz, stimulated a great deal of hydrothermal work as a result of which radically new equipment was developed. The availability of this equipment led many petrologists to tackle quantitative and equilibrium studies on a large scale the results of which are described below.

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EQUIPMENT

Research under high temperatures and high pressures is to a large extent only specialized insofar as the equipment is concerned. With the development of new and simple apparatus during the last few years a great expansion in activity may be anticipated. Equipment which has been developed for research in this field consists of both apparatus to generate the pressures of water or other fluid and the reaction vessels themselves.

The first category is more easily described than the second. Most laboratories doing such work have employed one of the following types of pressure generators:

I. Commercial pumps normally used for boosting gas or oil pressure (for example, those manufactured by American Instrument Co., Washington, D.C., and Autoclave Engineers, Inc., Erie, Pa.). These are ordinary piston-type pumps usually with ball and cone seats and can be used to a maximum of 4000 kg/cm^2 although they are rated for somewhat lower pressures. These pumps appear to be fairly suitable for short periods of time especially when required to maintain a steady pressure. Their chief disadvantages are the high initial cost and a susceptibility to small particles of dirt or rust becoming lodged in the valves and thus preventing operation of the pump.

II. Multiplying-piston type pumps working on the differential area principle utilizing laboratory compressed air. (A good example of this type is the pump made by the Sprague Engineering and Sales Co., Gardena, Calif.). The principal advantage of these pumps over the motor-driven type is that they automatically maintain an approximate control of the pressure by means of a simple regulator on the air pressure. They are usually cheaper by a factor of 4 or 5. They are usually limited to about 2000 kg/cm^2.

III. Pressure intensifiers: These are simple differential area two chamber arrangements usually used in conjunction with one of the other types of pumps to extend the range to about 5 to 6000 kg/cm^2. A laboratory pump utilizing an automobile jack (described by ROY and OSBORN, 1952a), and a single chamber for the fluid being compressed has been giving trouble-free operation for some years in a few laboratories for pressures up to 3500 kg/cm^2, and there seems to be no reason why it cannot be operated up to 10,000 kg/cm^2.

The second category includes the reaction chamber or "bombs". The types of vessels being used are gradually being narrowed down as experience shows which are the best. One can distinguish five basic types with several variations within each.

One of the earliest designs was that of SMYTH and ADAMS (1923 loc. cit., Fig. 1). This design was modified by GORANSON and later YODER (1950a) made

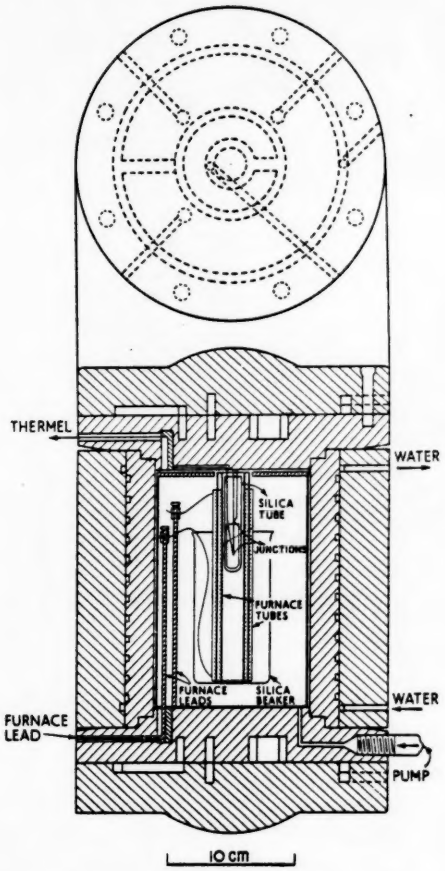

Fig. 1. Internally heated high pressure apparatus of the type designed by SMYTH and ADAMS (1923, ref. Fig. 1) and modified later by GORANSON and YODER. This type of vessel is capable of yielding runs at temperatures up to 1600°C and 10,000 kg/cm².

more drastic changes in design. This type of vessel has served as the vehicle for all the higher temperature (> 1000°C) or high pressure (> 4000 kg/cm²) work in the Geophysical Laboratory. It consists of a heavy-walled heat treated vessel of tool steel (usually 41–50 Cr—Mo) which contains the pressure, and an internal furnace and sample support. All the leads for the furnace and the thermocouples are brought in by means of a special packing. This equipment is

admirably suited for the study of reactions which can be studied by dynamic methods such as for differential thermal analyses at a series of pressures (e.g. the change of inversion temperature of quartz or the melting point of diopside), GIBSON, 1928, YODER (1950a loc. cit. and 1952a). In YODER's modification it is possible that temperatures of 2000°C may be attained although no data have been recorded at temperatures above about 1500°C. It cannot be used directly

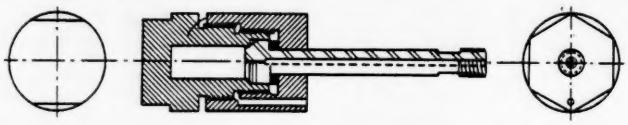

Fig. 2. Pressure vessel designed by MOREY typical of vessels in use in several laboratories for preparing larger samples, or working in acid and alkaline media.

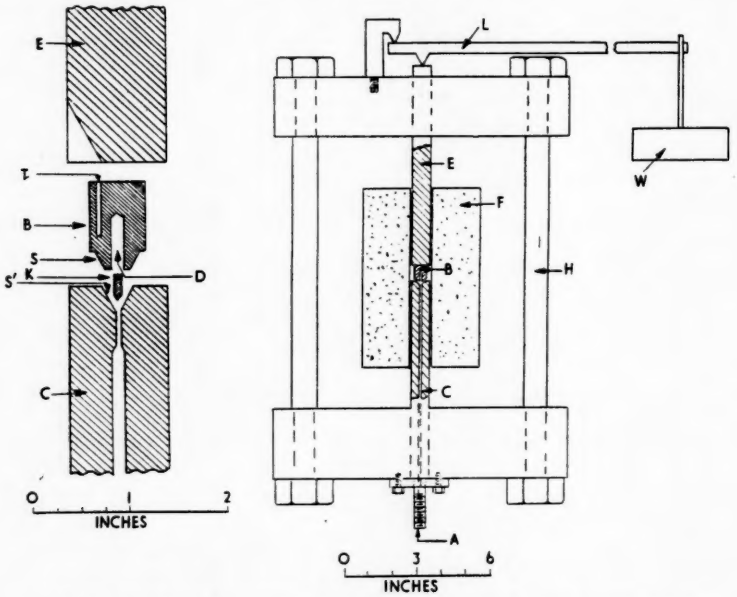

Fig. 3. Hydrothermal quenching apparatus designed by TUTTLE (1948). No threaded parts are heated, the seal being made by weights.

with water as the pressure transmitting fluid, but by sealing charges containing water in platinum tubes studies of such systems have also been made up to these temperatures (GORANSON, 1931, loc. cit.). This type of vessel is both expensive and cumbersome for most small scale laboratory experimentation.

In 1913 MOREY described a very simple vessel which has since been used extensively in all laboratories doing systematic hydrothermal work. This vessel has been modified in several respects and one of these forms is shown in Fig. 2 (see MOREY, 1953). The first versions of these bombs were sealed off with a fixed volume of water and the pressure was therefore fixed by the temperature. This was a serious limitation especially at temperatures below say 300°C, and

the most important modification was the introduction of a drilled plunger to introduce pressure from outside and later, utilizing a Bridgman seal (see MOREY, 1953 loc. cit.) these bombs have been used up to a maximum of 3 to 4000 kg/cm² up to about 600°C. Although for quantitative work they have largely been superseded, there is considerable use for them in most laboratories for preparing larger amounts of sample, and for dealing with soluble or corrosive components. For the latter case they have been successfully used with gold and silver liners, (FRIEDMAN, 1950) although MOREY himself has used very alkaline solutions in bombs made of Inconel X with no liner.

A different type of apparatus was designed by TUTTLE (1948) and it also has been modified by several users. It makes the basic advance of having no threaded

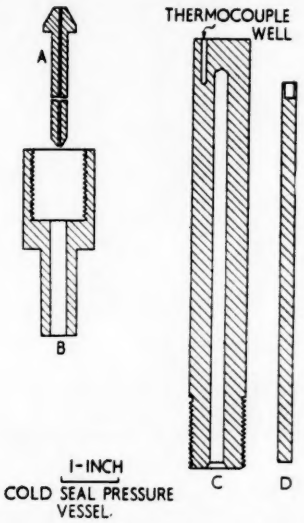

Fig. 4. The "cold-seal" or "test-tube" bomb (TUTTLE, 1949, ROY and OSBORN, 1950) the simplest and cheapest of the pressure vessels for temperatures up to 1000°C; it also affords the most efficient quenching.

parts which are heated, the seal being made by pressure (applied by weights) on a cone in cone seal. One version of this apparatus is shown in Fig. 3. The principal advantage of this type of apparatus is the simple construction and small size which permits more rapid quenching than with earlier externally heated vessels. The simple construction and small size of the pressure vessels permits rapid heating of the system so that runs can in general be made as rapidly as with the conventional technique used for anhydrous silicate systems. Thus this equipment is well suited for liquidus studies, particularly when the length of time required for equilibrium is relatively short.

The simplest pressure vessel, and the one which shows promise of most widespread use, was designed by TUTTLE (1949) and called "cold seal pressure vessel" (Fig. 4). This vessel is simply a cylinder of metal with an axial hole drilled from one end to within about 1 in. of the other end. The closed end is placed upward in a furnace with the pressure connection below and outside the furnace. Temperatures are measured with a thermocouple in a small well opposite the

charge. ROY and OSBORN (1950, 1952a loc. cit.) modified this vessel by suspending it in the furnace from above and they have used the name "test-tube" pressure vessel for this unit. The first type requires that the charges be supported by a rod within the vessel whereas in the latter type this is unnecessary. They may be made very cheaply out of ordinary stainless steel and are suitable at temperatures up to 750°C at 2000 kg/cm² for extended periods. By far the best alloy used to date, however, is "Stellite 25". This alloy enables one to reach 1150°C at 500 kg/cm² for an hour or so, and 900°C at 1000 kg/cm² indefinitely. When used with the closed end down, quenching by immersing in a bath of

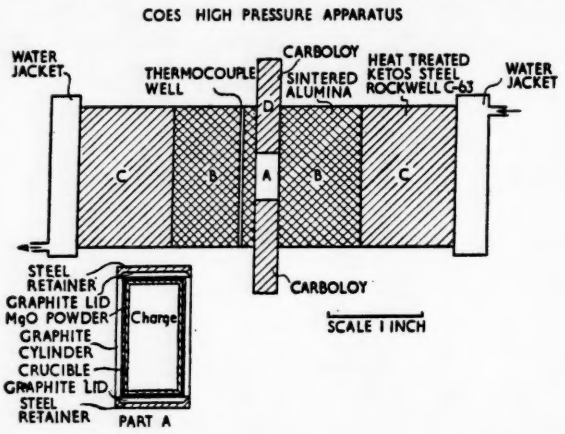

Fig. 5. Apparatus for sustaining pressures up to 45,000 kg/cm² at temperatures up to 900°C designed by L. COES, Norton Co., Worcester, Mass. (personal communication, 1954) and used in the first synthesis of several dense anhydrous minerals.

water is very efficient. The use of a close-fitting rod to decrease the volume of the vessel enhances the safety factor and greatly diminishes the effects of convection. These vessels have been used at pressures as high as 6 to 7000 kg/cm² at 700°C and there appears to be no reason why they should not be used to about twice this pressure (at suitably lowered temperatures). For higher pressures at elevated temperatures a radically different type of apparatus has been recently described.

This last type of apparatus has achieved such spectacular successes in the field of very high pressure mineral synthesis that it is certain that it will be the prototype of a large number of similar ones. The apparatus was designed and constructed some six years ago by L. COES at the laboratories of the Norton Co. in Worcester, Mass. based on BRIDGMAN's extensive experience with similar vessels (see BRIDGMAN, 1947; 1949). It is shown in print for the first time in Fig. 5. The parts are labelled and described in the figure. The principle utilized is very simple. The charge, enclosed in its silver or iron container, and surrounded by a graphite cylinder, is squeezed between two tungsten carbide pistons. The sample is heated by a low voltage current passed through the graphite cylinder—which although distorted greatly still acts as the resistor. This would of course not be possible except for the fact that the chamber surrounding the piston is of a non-conducting material (Alumina hot-pressed at 1800°C to theoretical

density). The pressure on the pistons is maintained in a large press with the pressure automatically controlled. This apparatus is very successful up to pressures of 35,000 kg/cm² at temperatures below 900°C for sustained periods of time. Runs have been made up to 45,000 kg/cm² at lower temperatures but the percentage of failures rises sharply under these conditions. The disadvantages of the apparatus are twofold. The temperature of the sample cannot be determined very precisely and moreover it may not be uniform throughout the sample. The pressure on the sample can only be calculated from the total pressure on the ram of the press, with allowances for the unknown coefficient of friction. However, at least approximate calibration has been achieved at the Bismuth transition, and BRIDGMAN has shown that the friction need not be a large factor.

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RESULTS OF STUDIES

Mineral Synthesis

It has already been mentioned that mineral synthesis has provided much of the stimulus for the renewed activity in this field, and although the results of this chapter are really concerned largely with the relationships between minerals or other phases, the interest in mineral syntheses appears to justify a separate section for their description.

It is now possible to say that virtually every common mineral known whether hydrated or anhydrous has been synthesized, and there is no reason to believe that the rarer minerals in which no interest has been shown will present any unsurmountable difficulties. This statement would have been considered pure fancy a year or two ago, the fact that it can now be made provides an indication of the rapid progress in the field. Very recently several organizations have announced the reproducible synthesis of diamond—long considered the final goal of mineral synthesis. Diamond can apparently be made quite rapidly if the conditions for its thermodynamic stability are attained. The G.E. (U.S.A.) group have used pressures near 53,000 kg/cm² and temperatures probably of the order of 1200°C. We list below by structural families the minerals in which there has been the greatest interest.

Silica Minerals

It is the growth of *large* quartz crystals rather than the synthesis of quartz which has been the subject of much research and now constitutes one of the "triumphs" of hydrothermal research. Following the work of NACKEN in Germany (1946, 1950) the Bell Telephone Laboratories and the Brush Development Laboratories in the U.S. and also Dr. W. A. WOOSTER and co-workers in Britain have made enormous strides in the field. The growth has now reached the commercial (though not economic) production stage in the Brush Development operation—output of some 1000 lb per month (of crystals averaging 200 to 400 g) having been achieved. Reviews of the development have been given by EITEL (1954, loc. cit.), WALKER (1953) and HALE (1948), and a growth mechanism has been proposed by CORWIN *et al.* (1953).

Other quartz-structure phases notably the orthophosphates have been studied in detail and grown hydrothermally, e.g. $AlPO_4$ (STANLEY, 1954). At least three

new phases having the total composition of SiO_2 have been reported—two of these having been prepared hydrothermally. COES (1953) reported a new dense form of SiO_2 (density 3·0) forming at pressures above 35,000 kg/cm² and KEAT (1954) reported another form prepared in the presence of alkalis (at pressures of a few hundred kg/cm²) with a general structural resemblance to high-spodumene. WEISS and WEISS (1954) reported still another fibrous form, which decomposes in contact with moist air.

Feldspars

While the high temperature forms of these minerals have been prepared in the laboratory fifty or more years ago, it is only very recently that the enormous complexity of feldspars has been recognized. The hydrothermal studies by BOWEN and TUTTLE (*vide infra*) have been instrumental in deciphering many heretofore puzzling relations among the alkali feldspars. Low-albite and -microcline which are very common in nature have not yet been synthesized but several other modifications have, and the complexities of cryptoperthitic intergrowths are gradually being deciphered. The subject is treated in detail in a later section.

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Dense Anhydrous Aluminosilicates

This group includes most of the metamorphic facies minerals, such as the garnets, sillimanite andalusite and kyanite, the epidotes, etc. No reproducible syntheses of these minerals had been achieved before the work of COES; in many cases this was in spite of a concentrated effort, e.g. the failure to obtain jadeite by YODER (1950b) and zoisite by EHLERS (1953). Andalusite was synthesized by D. M. ROY (1953) and the following minerals have all been made by COES (1953, personal communication, passim). A brief description of the conditions used is included.

Jadeite: by the reaction between sodium sulphate, kaolin and silica at a pressure of 20,000 kg/cm² at 900°C. Also with spessartite, from sodium permanganate, kaolin, and silica under the same conditions.

$NaCr(SiO_3)_2$: by reaction of sodium dichromate with silica at 20,000 kg/cm² and 900°C. This silicate crystallizes in deep green monoclinic crystals.

$\alpha = 1{\cdot}67, \beta = 1{\cdot}74, \gamma = 1{\cdot}76 +$
Biax. neg $2V = 40°$
Insoluble in HF. Sol. in fused NH_4HF_2

Andalusite: from kaolin in presence of sodium salts 20,000 to 30,000 kg/cm², 600 to 900°C.

Sillimanite: from kaolin in the presence of fluorides at 20,000 to 30,000 kg/cm², 600 to 900°C. There are indications of an extensive series of solid solutions from sillimanite to topaz.

Kyanite: forms easily as a by-product in a wide variety of systems containing Alumina and silica. 20,000 to 40,000 kg/cm² and 600 to 900°C. Can form simultaneously with sillimanite, and andalusite but not with topaz.

Topaz: same conditions as for sillimanite but higher fluoride contents. Best from kaolin and NH_4HF_2.

$Al_2O_3 \cdot 3SiO_2$: from hydrated alumina, aluminum nitrate and silica only at pressures above 45,000 kg/cm². The properties of this silicate are:

$$\alpha = 1{\cdot}67, \gamma = 1{\cdot}675$$
Biax. pos $2V = 90°$

Crystals are almost always twinned peculiarly and cleave across the waist leaving an irregular pentagonal plate.

Epidote Group

Epidote and Zoisite have been synthesized from hydrated calcium and iron nitrates, hydrated alumina and silica at 20,000 kg/cm² and 800°C.

Garnet Group

The following garnets hitherto not made in the laboratory have been synthesized in various ways:

Grossularite	at 15,000 kg/cm²	600–800°C
Andradite	at 20,000 „	600–800°C
Almandine	at 20,000 „	600–900°C
Pyrope	at 30,000 „	900°C
$Mg_3Fe_2(SiO_4)_3$	at 30,000 „	900°C
$Mn_3Fe_2(SiO_4)_3$	at 20,000 „	800°C
$Fe_3Fe_2(SiO_4)_3$	at 20,000 „	800°C
$Mg_3Cr_2(SiO_4)_3$	at 20,000 „	800°C

Minerals such as staurolite, chloritoid, beryl, datolite, vesuvianite, lawsonite and bertrandite have also been synthesized under similar conditions. Unfortunately very few data have been obtained on the equilibrium stability of these minerals and the pressures cited are not necessarily "required" in each case. The phases themselves are in most cases beautifully crystallized and in all cases unambiguously identified. Somewhat unusual starting materials have been used by COES in his work, e.g. a typical starting material for obtaining zoisite is: $Ca(NO_3)_2$, $Ca(OH)_2$ and SiC. In virtually all the runs a large number of additional components are present and there is no doubt whatsoever that these serve in many cases as essential "mineralizers" since the reaction does not proceed without them. The determination of equilibrium stability ranges for these minerals still constitutes a rather considerable problem, but one that can now be tackled more hopefully. Thus YODER (personal communication) has recently obtained quantitative information on almandine stability.

Other Anhydrous Phases

These include those phases which cannot be prepared by the "dry" reaction of the components. The low-temperature forms of the lithium aluminosilicates, spodumene, eucryptite and petalite were synthesized and their equilibrium relations studied by ROY, ROY and OSBORN (1950, loc. cit.) and similar results were also obtained by BARRER and WHITE (1951) with respect to the synthesis of the minerals. The rare gem mineral benitoite has been prepared by RASE and ROY (1955).

Micas

Much of the credit for early work on the layer lattice silicate synthesis is due to NOLL (1932, 1944) and GRUNER (1939, 1942). They were able to prepare

muscovite and paragonite from a variety of starting materials under hydrothermal conditions up to a maximum of about 400°C.

The typical end members of the mica group with ideal compositions such as muscovite (YODER and EUGSTER, 1953) phlogopite (YODER and EUGSTER, 1954) paragonite (SAND, ROY and OSBORN, 1953) and the tri-octahedral Ca mica (DEVRIES and ROY, unpublished) have been synthesized and in most cases a *p–t* curve describing their decomposition determined (vide infra). In addition, the polymorphism of these synthetic micas has been studied in detail by SMITH and YODER (1954). Synthetic phases approaching eastonite, annite and leucophyllite have also been prepared by YODER (personal communication). ROY and ROY (1954) have prepared a pure synthetic ferric analogue of muscovite.

Clays and Zeolites

Synthetic representatives of each of the clay mineral families have been known for some decades; the recent work is incidental to systematic studies and also new insofar as a very large variety of ionic substitution has been effected in these structures. Much of this work has been summarized by MOREY and INGERSON (1937, loc. cit.) and NOLL (1944, loc. cit.) and it is also referred to in a later section. The kaolinite-serpentine group has been studied in detail by ROY and ROY (1954, loc. cit.) and pure single phase clays of controlled compositions have been prepared and studied with respect to the relation between composition and properties. NOLL and KIRCHER (1952) synthesized garnierite and KARSULIN and STUBICAN (1951) claim to have synthesized halloysite although electron microscopic evidence was not presented. Montmorillonites within the system $MgO—Al_2O_3—SiO_2—H_2O$ have been studied in some detail by ROY and ROY (1952) and KARSULIN and STUBICAN (1954), and a large number of montmorillonites corresponding to the various naturally occurring types such as the saponites, beidellites, sauconites, hectorite, etc. have been prepared by these workers and by SAND and ROY (1953, unpublished). The chlorite family relationships have been greatly clarified by the synthesis of two isomorphous series of chlorites, with corresponding polymorphic members at each composition (NELSON and ROY, 1953). One series has a 7Å sequence of basal reflections and the other, higher temperature, higher pressure series corresponds to the more common 14Å series. Phases in each series with compositions corresponding to clinochlore, penninite, corundophyllite and amesite have been prepared. In later work Ni^{2+} and Cr^{3+} have been substituted into these phases (DEVRIES and ROY, unpublished) and the influence on x-ray reflections and equilibrium thermal stability studied.

The zeolites in the alkali-alumina-silica-water systems have been exhaustively studied by BARRER and co-workers (1951, loc. cit., 1952, 1953) and phases corresponding to the following minerals synthesized: analcite, mordenite, pollucite, rubidium analcite, and other zeolitic phases containing essential lithium with compositions near $Li_2O{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}4H_2O$ and $Li_2O{\cdot}Al_2O_3{\cdot}8SiO_2{\cdot}5H_2O$.

Lime-Silica-Hydrates

These are discussed in greater detail in a later section, but it should be mentioned here that phases corresponding to the natural minerals of afwillite, gyrolite, tobermorite, xonotlite, hillebrandite, have been prepared synthetically by JANDER

and FRANKE (1941), TAYLOR, *et al.* (1950–3) and KALOUSEK, LOGUIDICE and DODSON (1954).

Tourmaline

Ferruginous tourmalines have been synthesized by M. MICHEL-LEVY (1949) at relatively low-pressures and temperatures (500 kg/cm² and 500°C). The French group at the Sorbonne with A. MICHEL-LEVY, including J. WYART and M. C. MICHEL-LEVY (see e.g. 1946, 1947, 1949) have utilized the explosion of organic materials to generate pressure in their high temperature—high pressure work: this makes it fairly easy to attain quite high pressures (up to 50,000 kg/cm²) but quantitative work is prohibited. This group has also synthesized a number of other hydrated and anhydrous minerals such as the feldspars, brucite, biotite, jeremejevite ($AlBO_3$), garnets, sillimanite (?), topaz, etc.

Tourmaline has also been synthesized under similar conditions by F. G. SMITH (1949) and FRONDEL *et al.* (1947) "re-synthesized" it from a glass formed by melting a natural tourmaline.

Uranium Minerals

In an extensive attempt to synthesize and classify the uranium minerals, GRUNER (1952) has prepared a large number of the common uranium minerals under conditions of varying pH, temperature (from room temperature to 250°C) and pressure. Minerals such as curite, uraninite, soddyite, kasolite, clarkeite, fourmarierite have been prepared under these conditions although very little information on stability is as yet available.

Sulphide and Other Minerals

A considerable volume of work has been done under hydrothermal conditions yielding minerals which could also be prepared dry: e.g. the work of GILLINGHAM (1948) in which anhydrous phases such as wollastonite and forsterite were obtained in addition to hydrated phases. Many sulphide minerals can similarly by synthesized "dry" and up to the present date most quantitative work on the sulphides has been done in the absence of water. We have therefore not dealt with such work (e.g. the extensive work of F. G. SMITH) which falls in these categories.

PHASE EQUILIBRIUM DATA

Some forty years ago the systematic study of phase equilibrium in high temperature silicate systems was initiated at the Geophysical Laboratory in Washington and scarcely 10 years after the beginning of this work N. L. BOWEN developed his petrologic ideas based on these phase equilibrium data. These ideas—though not universally accepted—have without question been one of the rare landmarks in the history of petrology. The extrapolation of experimental phase equilibrium results based on the data obtained from systems made from relatively few and chemically pure components to natural systems has of course been open to criticism. During succeeding years more and more complex systems have been studied and these have in some measure improved the situation. However, one of the chief criticisms has been that in these laboratory studies no water has been present—and this oxide may alter the relationships drastically. Further, of course, the addition of water as a component to the phase equilibrium studies would also make it possible to study relationships

involving mineral phases in which essential water (or more often OH^-) is present. Although—as can be seen from the earlier sections a considerable amount of mineral synthesis work had been done in the twenties and thirties, with the exception of the work of GORANSON (loc. cit.) and MOREY no systematic phase equilibrium work had been attempted before the second World War. It was not till some years after the war that phase equilibrium data involving water-containing systems began to accumulate. The "dry" melt data have proved to be of considerable significance in both petrology and ceramic technology and it is natural to expect that the data from the hydrothermal systems will also prove of value in the same fields.

These phase equilibrium data will be described in two sections, the first being largely descriptive of the results obtained and involving those systems in which no liquid-phase (apart from water) is formed, and the second indicating the areas in which these results apply to petrology and geochemistry and describing those systems where the liquidus relationships have been studied. A word needs also to be said about the method of representation of the results. Since in most of the former type of studies described we are concerned with the relationships among the solid phases, those methods have been used which show up these relationships most clearly. Very little of the recent work has been described in terms of the solubility of the components in water, and especially where the common rock forming minerals and oxides are conerned, the solubility is so low (always within a few tenths of a per cent) that it appears justifiable to show the only fluid phase as having the composition of pure water. With the use of two sets of diagrams all the useful data obtained from these phase equilibrium studies of binary, ternary and quaternary systems may be conveniently represented. The first representation describes by means of a subdivided set of ternary composition triangles the stable phase assemblages present at a sequence of significant temperatures at any chosen pressure, i.e. a study of two contiguous triangles indicates graphically the nature of the reaction taking place at the temperature involved. The second diagram consists of a series of univariant curves relating the temperature at which these reactions take place to the water pressure. Of course in binary systems and in ternary systems it is possible to combine these representations by showing the triangles on the same diagram as the *p–t* curves. Many workers have followed the pattern set by BOWEN and TUTTLE (1949) in their pioneering work on the system $MgO—SiO_2—H_2O$. The concept of "water-deficiency" which must be borne in mind when discussing these data is also discussed in this paper. Briefly, this concept defines the limits imposed by present-day experimental techniques on the compositional region which can be studied. It implies that one cannot obtain direct evidence on the stability of phase assemblages in the presence of water vapor when all the phases in equilibrium are solid; in other words, experimental data are obtained only on those binary joins, ternary triangles or quaternary tetrahedra which involve water as a phase. For details of the concept the original paper should be consulted; it has also been treated by YODER (1952b) and ROY (1953). It is important to emphasize that in all the work done to date, the "pressure" is always the pressure of the volatile, if any, which is involved in the reaction. The whole question of how these results relate to geological phenomena where independent "rock pressures" and "fluid pressures" may exist has so far been hardly touched. The experimental difficulties in the way of testing any hypotheses are so con-

siderable that discussions of this problem will for a while have to be confined to theory. The work of DANIELSSON (1950) and MACDONALD (1953) is of considerable interest in this connection.

Pressure-Temperature-Volume Relations for H_2O *and* CO_2

Important new data on the *p–v–t* relations of water have been obtained by KENNEDY (1950a); these supersede the earlier data of VAN NIEUWENBURG and BLUMENDAHL (1932) and the steam tables of KEENAN and KEYES. They have

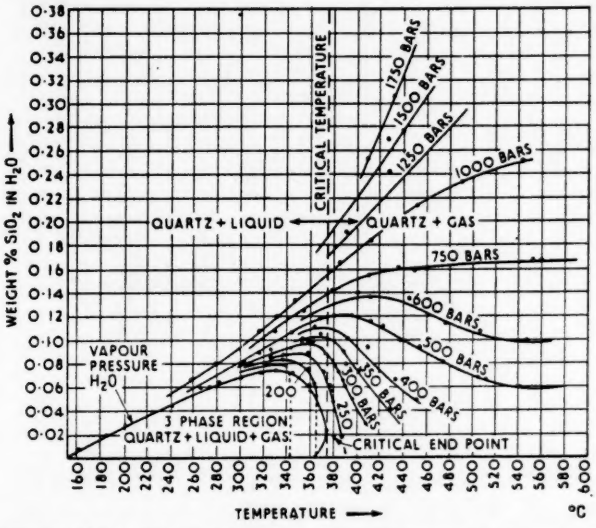

Fig. 6. Solubility of SiO_2 in H_2O as a function of temperature and pressure, after KENNEDY.

been extended up to 1000°C and 2600 kg/cm² in pressure, and therefore prove invaluable both in experimental work, and in the calculations involving water under these conditions. KENNEDY has subsequently (1954) obtained similar data for CO_2 up to 1000°C and nearly 1500 kg/cm².

Subsolidus Studies

Most of the post-war hydrothermal studies have been carried out at temperatures and pressures below that at which a liquid (melt) phase appears and above the critical temperature of water. These studies are therefore concerned largely with crystal ⇋ vapour equilibria.

The System SiO_2—H_2O: Solubility measurements in this system have been recently carried out by KENNEDY (1950b), and MOREY and HESSELGESSER (1951) and these describe the pressure and temperature dependence of the solubility. The most interesting feature is the maximum in solubility shown at pressures below about 500 bars; this maximum being sharper at lower pressures as seen in Fig. 6.

The effect of water vapour pressure on the quartz-tridymite inversion has been studied by TUTTLE and ENGLAND (1955). It should be pointed out that the experimentally determined slope of the univariant *p–t* curve (see Fig. 7) differs markedly from the calculated curve of MOSESMAN and PITZER (1941) which was

based on thermo-chemical measurements. The slope dp/dt for the quartz-tridymite inversion was found by TUTTLE to be about 6 kg/cm²/°C which is approximately four times as steep as the calculated p–t curve. It was also shown that quartz will melt directly to a liquid at water pressures above approximately 1400 kg/cm² at temperatures near 1125°C.

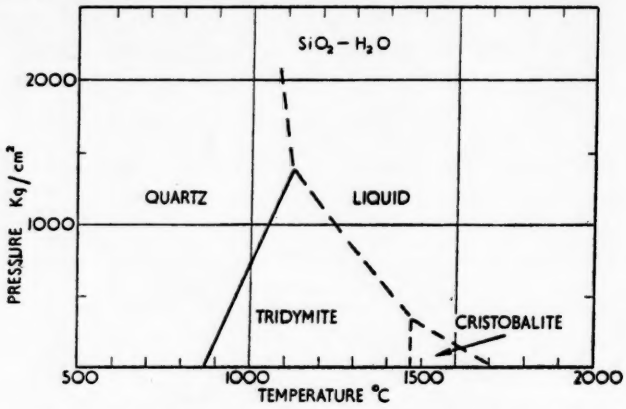

Fig. 7. Part of the system SiO_2—H_2O, pressure is water pressure. TUTTLE and ENGLAND, 1955.

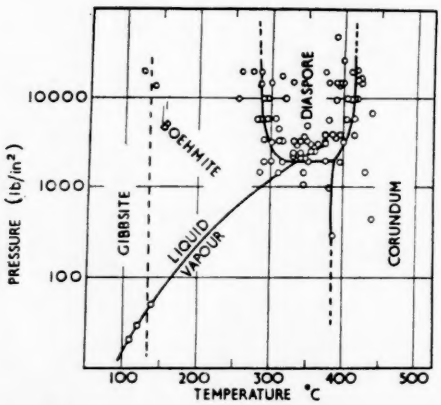

Fig. 8. p–t diagram for the system Al_2O_3—H_2O, after ERVIN and OSBORN, 1951.

The System Al_2O_3—H_2O: Equilibrium studies on this system have been made by LAUBENGAYER and WEISZ (1943) and more thoroughly by ERVIN and OSBORN (1951). The form of the equilibrium diagram, after the latter authors, as a set of p–t curves, is shown in Fig. 8. The remarkable feature of this diagram is the fact that diaspore which is the denser of the two polymorphs of composition $Al_2O_3 \cdot H_2O$ appears at the higher temperature. Because of the inverse density relationship the slope with pressure is also reversed and results in the crossing of this curve with the decomposition curve of boehmite. The further result of this relationship is that diaspore is therefore stable only above about 150 kg/cm².

This result appears to be unacceptable to many field geologists (see for example KELLER, 1952) but other experimental evidence from equilibria in the system Al_2O_3—Ga_2O_3—H_2O appears to confirm it (HILL, ROY and OSBORN, 1952). It should of course be borne in mind that the fact that diaspore is only stable above (270°C and) 150 kg/cm² does not preclude its metastable formation and certainly not its metastable persistence after it has been formed. However, one consideration against the possibility of the metastable formation of diaspore is its higher

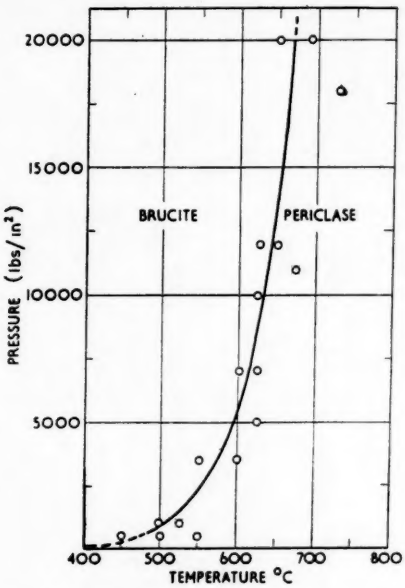

Fig. 9. *p–t* diagram for the reaction $Mg(OH)_2 \rightleftarrows MgO + H_2O$, after ROY, ROY and OSBORN.

density when compared to boehmite, since the metastable formation of the high density phase appears to be prohibited.

The System MgO—H_2O: This system has received a great deal of attention during the last several years. Extensive earlier work has been reviewed by FRICKE and HUTTIG (1937). GIAUQUE and ARMSTRONG (1937) studied the system at low water vapour pressures and later GIAUQUE (1949) presented a most important paper considering the application of thermodynamic parameters obtained from thermochemical measurements on "large" crystals to calculations in such work. Conversely, therefore, the determination of such parameters by the treatment of *p–t* data is quite definitely limited with respect to accuracy when compared with other values obtained on "macro" crystals.

The major differences which exist in the literature on the equilibrium data for the reaction $Mg(OH)_2 \leftrightharpoons MgO + H_2O$ demonstrate the limitations of much of the hydrothermal work to date. Most recently the system has been studied by BOWEN and TUTTLE (loc. cit.) and ROY, ROY and OSBORN (1952) by static methods; and by dynamic methods by the Russian workers under V. I. LEBEDEV (1952) and personal communication (1954).

The curve presented in Fig. 9 is from the work of ROY, ROY and OSBORN and is possibly the most nearly correct at high pressures. It should be noted that ΔH values for the reaction obtained from this curve at about 500 kg/cm² are near 15,000 cals/mole whereas GIAUQUE obtains a value of 9739 cals/mole $\pm$ 25 cals at about 50 mm pressure and 200°C (water as liquid). Other literature values vary up to 23,500 cals/mole at room temperature, and not all these

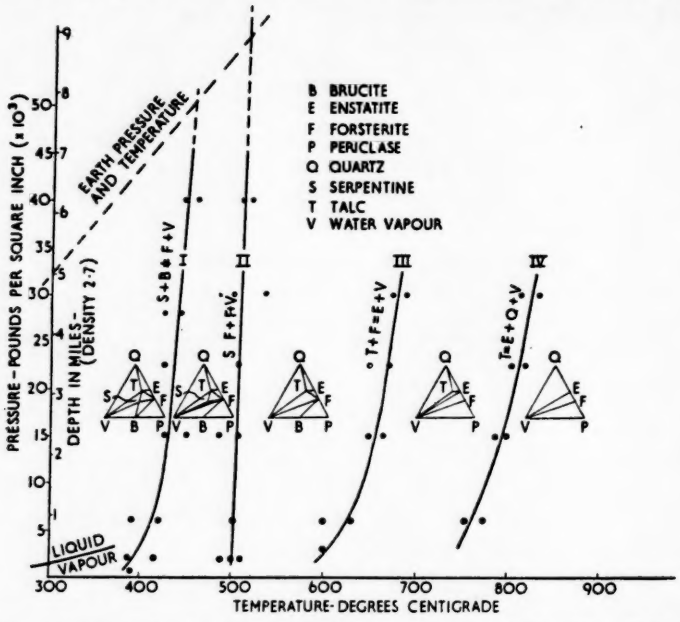

Fig. 10. *p–t* curves of univariant equilibrium in the system MgO—SiO_2—H_2O after BOWEN and TUTTLE (1949), with brucite decomposition curve omitted to avoid complication. The lower left curve is the vapour pressure curve of water ending at the critical temperature and pressure. The upper left curve is the curve of normal earth pressure and temperature, assuming a density of 2·7 and a temperature-gradient of 55°C/mile.

variations can be ascribed to differences in the heat content of the MgO formed, which in the case of the sample studied by GIAUQUE amounted to about 900 cals (when compared to another unrelated sample used for thermochemical measurements).

The System MgO—SiO_2—H_2O: This was the first ternary system to be completely investigated and in many respects laid the groundwork for much of the recent work. BOWEN and TUTTLE (1949, loc. cit.) describe the change of assemblages with temperature and also show the effect of pressure on the temperatures involved. A composite diagram expressing all the data is shown in Fig. 10. Several important reactions were involved in the system, e.g.:

The serpentinization of forsterite (olivine).

The decomposition of the two layer-silicates, chrysotile and talc.

The reaction of forsterite and talc to yield enstatite and water vapour (or the stability limit of enstatite in the presence of water).

It was shown that forsterite would be serpentinized at 400°C (at pressures of about 500 kg/cm²) and that if 10 per cent of fayalite was present in the molecule this would take place some 80°C lower.

In the same pressure range the serpentine persists to a maximum of about 500°C and talc to 780°C. With a geothermal gradient of 55°/mile this would mean that serpentine cannot exist at all below a depth of about nine miles in the earth. One of the important conclusions from the data is the fact that a dunitic

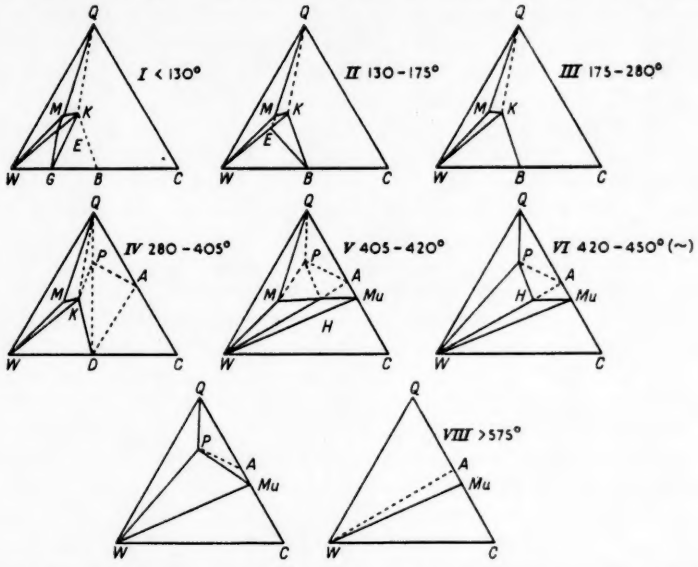

Fig. 11. Sequence of composition triangles showing stable phase assemblages in the system Al_2O_3—SiO_2—H_2O for a pressure of about 700 kg/cm². Solid lines show assemblages experimentally determined, dashed lines show other probable relationships.

A = andalusite, B = boehmite, C = corundum, D = diaspore, E = endellite, G = gibbsite, H = hydralsite, K = kaolinite (nacrite, dickite or halloysite), M = montmorillonite, Mu = mullite, P = pyrophyllite, Q = quartz, W = water.

magma containing even large amounts of water would not exist at 1000°C (and probably not for several hundred degrees more) nor would a peridotitic composition near serpentine call for melting at these temperatures.

The System Al_2O_3—SiO_2—H_2O: Earlier work on the stability relations in this system was largely that of NOLL (1935, 1937, 1944, loc. cit., etc.). This excellent early work—probably the best of the pre-war subsolidus work—first disclosed the outlines of the stability relations in this system. At the time of the study, however, insufficient data were obtained over a relatively narrow range of temperature and pressure conditions to permit much generalization on the equilibrium relations in the system. A more exhaustive and detailed study was carried out by ROY and OSBORN (1949, 1954). The results are presented in Fig. 11 in a form similar to those in the system MgO—SiO_2—H_2O described above, showing the sequence of phase-assemblages as a function of temperature at one pressure. The *p–t* curves have not been reproduced since they are very steep

within the range of the experiment. It is interesting to compare these data with those of NOLL and to note the similarity in broad outline. The system is of basic importance not only for metamorphic petrology but also for the understanding of the clay mineral relationships. The data obtained are disappointing insofar as the metamorphic minerals are concerned since it was not possible even to synthesize kyanite, sillimanite and andalusite. Assuming the validity of these data would mean that these minerals will only appear as stable phases *under these conditions* at much higher pressures (> 3000 kg/cm^2). The other relationships in the system have, however, been greatly clarified. Thus the *p–t* curve for the decomposition of endellite ($Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$), (see also SAND, 1952) shows that it is meaningless to state that endellite dehydrates at a certain temperature unless the water vapour pressure is also specified. The confusion has arisen largely from the fact that the decomposition curve lies very near to the saturation curve of water and that while endellite will dehydrate in a cold dry room, it can persist up to nearly 200°C at 2000 kg/cm^2 water pressure. The *p–t* curve for the kaolinite minerals shows very little slope (not more than 10 to 15°C) between pressures of 300 and 2000—3000 kg/cm and a maximum temperature for this family is therefore fairly near 400°C for any burial ranging from $\frac{1}{2}$ to 5 miles or more. Dickite and nacrite have not been reproducibly synthesized and it is not unlikely that they will require higher pressures than have so far been used; they decompose (metastably) to the same products as are formed from kaolinite—pyrophyllite + hydralsite + H_2O—at essentially the same temperature as kaolinite. Hydralsite is a new synthetic phase which has not as yet been found in nature but which could have been mistaken for pyrophyllite. The pyrophyllite decomposes at 575°C at 1000 kg/cm and in this case also the change in this temperature (as far as the experimental data go) is surprisingly small for several fold changes of pressure above about 300 kg/cm^2. It is worth noting that the dioctahedral members of the various layer silicates invariably decompose at lower temperatures than their trioctahedral counterparts thus kaolinite 400°C, serpentine 500°C; pyrophyllite 575°C, talc 780°C; muscovite 650°C, phlogopite 1025°C (at corresponding pressures). An important conclusion from the equilibrium work in this system is the fact that a ceramic body lying in the system (and a large number do) can be completely reacted by "firing" to a maximum of 575°C—nearly 1000°C lower than the temperatures often used for some products in this system.

The System $MgO—Al_2O_3—H_2O$: This system has been studied by ROY, ROY and OSBORN (1953, loc. cit.) and since insufficient data were obtained to determine significant *p–t* curves, the phase assemblages are shown in Fig. 12 with their temperature range of stability indicated for a pressure of 350 kg/cm^2. Apart from the brucite—periclase transition, the most important reaction is perhaps that of the decomposition of spinel by water at temperatures below 365°C (at this pressure). The addition of CO_2 to this system yields the possibility of forming the minerals hydrotalcite and hydromagnesite, both of which were encountered. The latter mineral decomposes at about 185°C for pressures near 700 kg/cm^2; whereas the equilibrium temperature for the reaction hydrotalcite $\leftrightharpoons$ magnesite + brucite + diaspore + H_2O appears to vary less than 20°C from 150 to 1400 kg/cm^2 being 325°C at 350 kg/cm^2, and appears to be hardly affected at all by variations in partial CO_2 pressure from virtually nil to 150 kg/cm^2 and 700 kg/cm^2. An interesting nitrate analogue of hydrotalcite was also encountered

and found to be stable to approximately 100°C higher temperatures than the carbonate member.

The System FeO—SiO_2—H_2O: This system has been described by FLASCHEN

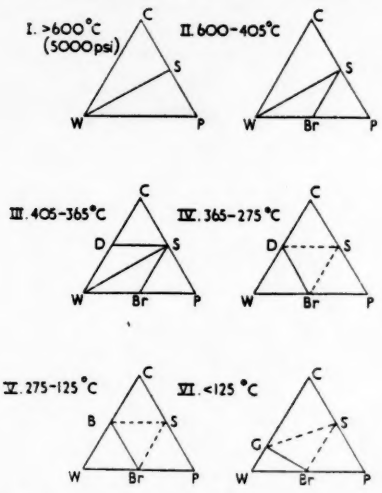

Fig. 12. Sequence of triangles showing stable phase assemblages at indicated temperatures for the system MgO—Al_2O_3—H_2O after ROY, ROY and OSBORN (temperatures shown for pressure of approximately 350 kg/cm³).

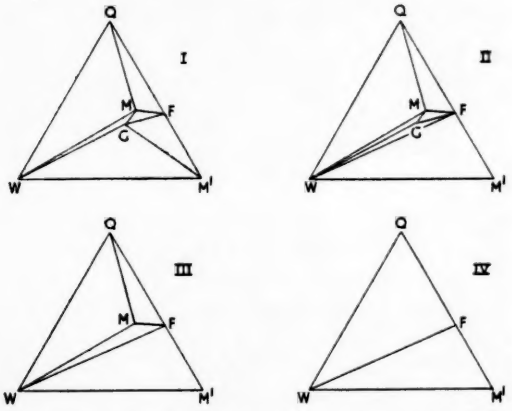

Fig. 13. Sequence of triangles showing stable phase assemblages in the system FeO—SiO_2—H_2O after FLASCHEN and OSBORN. At a pressure of approximately 1000 kg/cm² the temperatures of the reactions involved are:

I → II at 250°C; II → III at 465° C; III → IV at 480° C. Q_1 = quartz, M = minnesotaite, G = greenalite, F = fayalite, M = Fe_xO_y.

and OSBORN (1953) the results having been obtained by working in a closed system in the presence of a partial hydrogen atmosphere. The serpentinization of fayalite is found to occur at about 250°C for pressures from 100 kg/cm² to

about 1200 kg/cm² (cf. 400°C for forsterite) and the maximum temperature for the ferrous analogue of serpentine—greenalite—was found to be about 465°C (cf. 500°C for serpentine) while the talc analogue—minnesotaite—decomposed at 480°C under the same pressures (cf. 780°C for talc). These data are summarized in Fig. 13.

The System $CaO—Al_2O_3—H_2O$: The early phase equilibrium data on this system with regard to the solid phases being formed at varying temperature and pressures are very sketchy indeed. However, a large volume of data has been

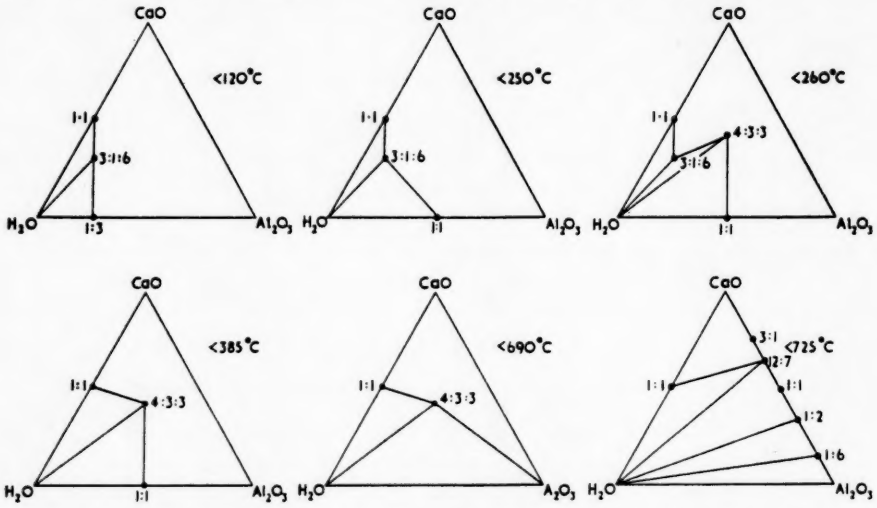

Fig. 14. Phase equilibria in the system $CaO—Al_2O_3—H_2O$ after MAJUMDAR and ROY (*Bull. Amer. Ceram. Soc.*, **34**, p. 9, 1955). The stable assemblages are shown at a pressure of 10,000 psi. From the final triangle it can be seen that $Ca(OH)_2$ decomposes at 725°C at 10,000 psi (H = 23,000 cals/mole) and also that both $CaO·Al_2O_3$ and $3CaO·Al_2O_3$ have minimum temperatures of stability which have been shown to be above 1000°C.

accumulated by WELLS and co-workers (1943, 1954) on the composition of solutions in equilibrium with solid phases as a function of temperature. THORVALDSON and co-workers (1943) have obtained similar data but have also prepared certain other phases under different temperature-pressure conditions. In a recent study MAJUMDAR and ROY (1955) have obtained more extensive data including *p–t* curves for $Ca(OH)_2$ and ternary hydrates. Fig. 14 shows the equilibrium relations at ca. 700 kg/cm². The stability minima of $CaO.Al_2O_3$, and $3CaO.Al_2O_3$ are most interesting.

The System $CaO—SiO_2—H_2O$: Due to the importance of phases in this system in the cement industry, a very large volume of work has been done at low temperatures and low pressures. Since it is difficult under such conditions to obtain anything approaching equilibrium, many of the data are confusing and conflicting. In addition the problem in this system is complicated by the existence of a very large number of phases, many of which have not been fully described or catalogued. The number of phases will run at least as high as twenty with over half that number being ternary hydrates. BOGUE (personal

communication) has summarized much of the earlier work and has prepared a valuable list of the compositions and properties of most of the compounds in the system. The most important recent contributions have been those of H. F. W. TAYLOR and co-workers (1950, 1953, loc. cit.). They have to a considerable extent untangled the threads of the composition, properties and nomenclature of the natural minerals occurring in this system. In addition they together with a very large number of earlier workers have made hydrothermal runs on synthetic mixtures in the system. Much of this work has been summarized by STEINOUR (1947) and most recently by TAYLOR *et al.* (loc. cit. and 1952).

The best data obtained to date appear to be those of FLINT, MCMURDIE and WELLS (1938) and apart from this excellent early work however, no serious attempt has been made to obtain either equilibrium assemblages or *p–t* curves for particular reactions. This may be ascribed mainly to the very difficult nature of the problem, due both to the large number of phases involved, the low temperatures of the reactions, and the very marked metastability phenomena encountered. A high temperature, high pressure study of the system by D. M. ROY, D. BUCKNER and R. ROY is now in progress. A *p–t* curve for the reaction xonotlite $\leftrightharpoons$ β-$CaSiO_3$ + H_2O showing equilibrium at 425°C and 2000 kg/cm² and about 400°C at 500 kg/cm² has been obtained in good agreement with the data of FLINT *et al.* (1938). The inversion temperature of $\gamma \leftrightharpoons \alpha'$ Ca_2SiO_4 has been lowered from 850°C to ca. 750°C, and least two new phases (one hydrated) at the 2CaO : SiO_2 ratio have been encountered. The few other stability data are best summarized by TAYLOR (1952, loc. cit.).

The Systems K_2O—SiO_2—H_2O and Na_2O—SiO_2—H_2O: Portions of the potash system constitute one of the earliest and most thoroughly investigated systems. In addition to the usual problems associated with hydrothermal systems the alkali containing systems present one extra technical and one theoretical problem. The corrosive nature of the liquids makes the equipment problem doubly difficult. In addition, the liquid and gaseous phases may now no longer be considered as pure water since large amounts of the potassium silicates may be dissolved in them. The temperatures involved are low enough that melting phenomena also appear thus complicating representation: these results are described in a later section.

The Systems BaO—Al_2O_3—H_2O and SrO—SiO_2—H_2O: A preliminary survey of the compounds in these systems has been reported by CARLSON and WELLS (1948) and a later study of equilibrium at 30°C by CARLSON, CHACONAS and WELLS (1950). A study of the compounds in the system SrO—SiO_2—H_2O has also been published by CARLSON and WELLS (1953) and these have been compared with the calcium silicate hydrates, few analogous structures being found.

Among the quaternary systems only one has been worked out in relative detail—MgO—Al_2O_3—SiO_2—H_2O. The alumino-silicate systems with the alkali oxides have been partly worked out, but almost no work has been done in the system CaO—Al_2O_3—SiO_2—H_2O which appears to be extremely complex and difficult to study.

The System MgO—Al_2O_3—SiO_2—H_2O: This system was studied simultaneously by ROY (1952) and YODER (1952b, loc. cit.) and later work has been done in the system by ROY and ROY (1955), NELSON and ROY (1954, loc. cit.) and ROY and ROMO (1954). When the system is described by a sequence of composition triangles showing stable assemblages, one component must

necessarily be excluded from the composition and the compositions are therefore shown projected on the anhydrous base. The sequence of triangles shown in Fig. 15 taken from ROY and ROY (1955, loc. cit.) incorporates the work of YODER (1952, loc. cit.). It will be seen that the mineral phase assemblages

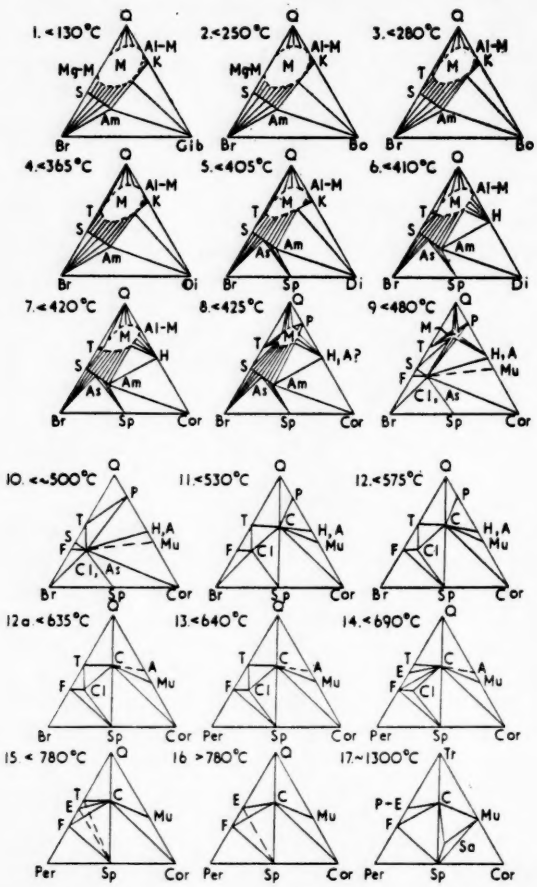

Fig. 15. Sequence of triangles showing stable phase assemblages in the system $MgO—Al_2O_3—SiO_2—H_2O$ and the variation with temperature (at 1000 kg/cm² water pressure) after ROY and ROY incorporating the work of YODER. Triangles after No. 8 have been simplified by neglecting solid solution in the 14Å chlorite phase. Later work by NELSON and ROY has shown that these chlorite solid solutions are stable up to the amesite composition and hence some modification of these triangles is necessary.

represent a transition—as we increase temperature—from the typical clay mineral assemblages of many sediments through the metamorphic assemblages to the high temperature assemblages found in the thermal-shock-resistant ceramic porcelains. The applications of these data in clay mineralogy have been discussed by ROY *et al.* in the above papers while YODER (1952b, loc. cit.) has given a thorough discussion of the application to problems of metamorphic

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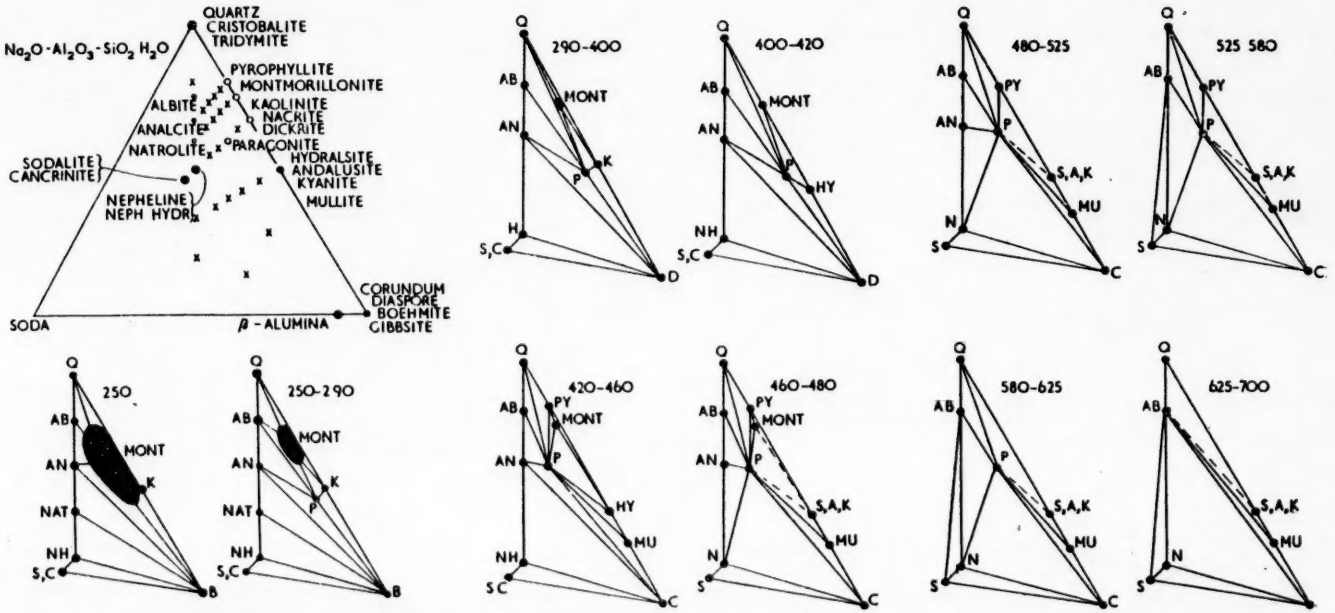

Fig. 16. Sequence of stable phase assemblages in the system Na_2O—Al_2O_3—SiO_2—H_2O obtained at successively higher temperatures (indicated for a pressure of 1000 kg/cm²) by SAND, ROY and OSBORN, incorporating the data of BARRER *et al.* The compositions of the phases are shown correctly in the first figure, the other triangles are distorted for clarity.

petrology. It should be noted that the synthesis of pyrope by COES (loc. cit.) will change these triangles considerably, at least at higher pressures and perhaps even at the pressures indicated.

The Systems Alkali—Al_2O_3—SiO_2—H_2O: Of these systems the soda system has received much more attention than any of the others. BARRER *et al.* (1952, loc. cit.) synthesized a large number of phases in the system, while SAND, ROY and OSBORN (1953, loc. cit.) had initiated an equilibrium relation study encountering most of the same phases. FRIEDMAN (1951) also made a study of the composition of the liquids in the soda-rich portion of the system not studied by the other

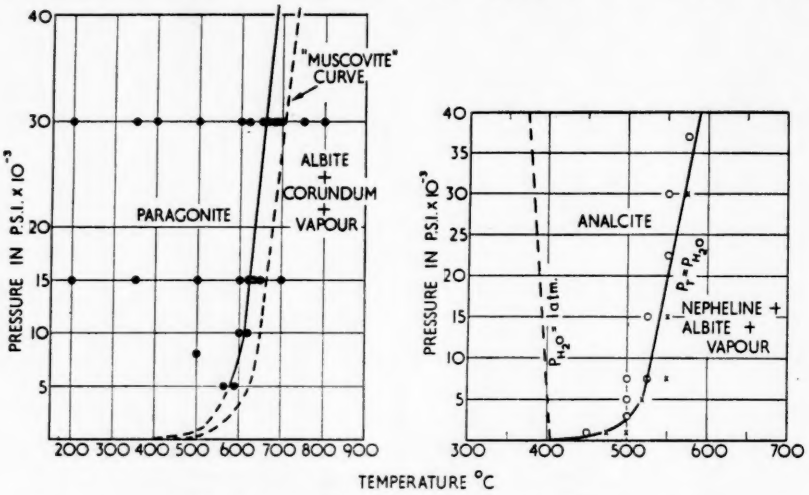

Fig. 17. *p–t* curve for the dehydration of analcite to nepheline + albite + vapour (YODER, personal communication) and of paragonite to albite + corundum + vapour, after EUGSTER and YODER.

investigators and found two new phases rich in soda. EUGSTER and YODER (1954) studied one reaction among those involved in the system in detail, namely the decomposition of paragonite $\leftrightharpoons$ corundum + albite + H_2O, as a function of temperature and pressure. Their values agree generally at the corresponding pressure with the values obtained from the sequence of triangles shown in Fig. 16 taken from the work of SAND, ROY and OSBORN (1953, loc. cit.).

In addition to this work MOREY (1947, unpublished) studied the decomposition of analcite—although the data obtained were probably not equilibrium values as shown by SAND, *et al.* (1953, loc. cit.). YODER (personal communication) has since obtained a more detailed *p–t* curve for the analcite decomposition (Fig. 17). Also shown in Fig. 17 is the *p–t* curve for the decomposition of paragonite.

YODER's exhaustive study of the jadeite problem (1950b) and the attempts to synthesize it—although abortive—have increased our knowledge of the system. Here again the synthesis of jadeite by COES, indicates probably that drastic revision of Fig. 16 will be required at least above 20,000 kg/cm^2.

In the potash system initial work by DEVRIES and ROY (1953, unpublished) showed the absence of any hydrated phases excepting muscovite which is also

absent above about 650°C. This mineral's decomposition reaction has been studied in detail by YODER and EUGSTER (1953, loc. cit.) and the results are shown in Fig. 18.

YODER and EUGSTER (1954, loc. cit.) have also obtained the important p–t curve describing the equilibrium dehydration of phologopite also shown in Fig. 19 and it is interesting to note the increase in thermal stability over muscovite. They have extrapolated their high-pressure data to a pressure of one

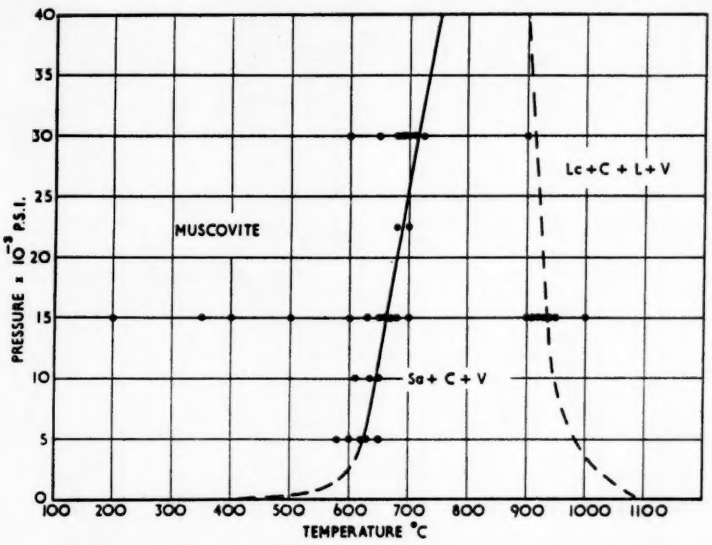

Fig. 18. p–t curve for the dehydration of muscovite to sanidine + corundum + vapour and the effect of water pressure on the "melting point" of muscovite, after YODER and EUGSTER.

atmosphere by use of the van't Hoff isochore and obtained a value of 770°C for the equilibrium temperature.

In this excellent study the authors have also presented data on the polymorphism of the phlogopites and attempts were made to determine pressure-temperature relationships among the polymorphs, but these were unsuccessful. The relation of the presence of phlogopite-biotite in both intrusive and extrusive basalts is explained by comparison of the dehydration curve with the minimum melting curves of "granite" and "basalt".

DEVRIES and ROY (1954, unpublished) have studied the decomposition of the Ca analogue of phlogopite—which can be prepared synthetically and also occurs naturally as the mineral seybertite (?). The dehydration temperature is found to be 300 to 400°C lower than that for phlogopite. In the lithia system ROY, ROY and OSBORN (1950, loc. cit.) made the first study of the subsolidus phase-relations of the anhydrous ternary compounds (but not of the hydrated zeolitic materials) in attempting to present a more complete phase diagram of a "dry" system (Fig. 20). The same phases were described and studied by BARRER (1951, loc. cit.). BARRER *et al.* (1952, 1953, loc. cit.) have also prepared the hydrated

zeolite phases in the Li_2O, Na_2O, Rb_2O and Cs_2O system and described their properties and given the general pressure and temperature conditions for formation of these phases.

In the system $CaO—Al_2O_3—SiO_2—H_2O$ only specific problems have been tackled: for example, YODER's exhaustive study of the grossularite problem (1950) and the related work of FLINT, MCMURDIE and WELLS (1941, loc. cit.) on the hydrogarnets. Although anhydrous grossularite was not obtained in either

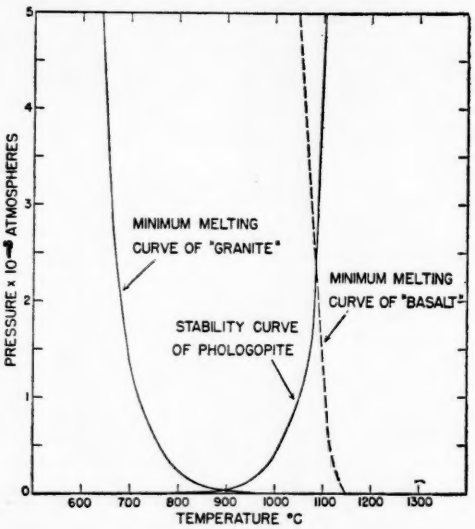

Fig. 19. *p–t* curve for the reaction 2 phlogopite $\rightleftarrows$ 3 forsterite + leucite + orthorhombic $KAlSiO_4$ + $2H_2O$. Also shown are the "minimum melting" curves of "granite" and "basalt", after YODER and EUGSTER.

of these studies YODER has determined the relations in a oblique plane in the *p–t–x* prism for the system grossularite-water. This leads to the interesting condition where the higher water content phases are stable at higher temperatures. DEVRIES and ROY (1954, unpublished) studied the decomposition of margarite to anorthite + corundum + vapour as a function of temperature and water pressure; they were unable to synthesize the phase in their work (which was limited to 3000 kg/cm²) and obtained on a natural sample decomposition temperatures of 590°C at 2000 kg/cm² and ~ 540°C at 500 kg/cm².

Nepheline-Kalsilite Relations

TUTTLE and SMITH (1953) have studied the subsolidus phase relations in the system nepheline-kalsilite. Perhaps the most important result of the study is the location of a miscibility gap between the two phases kalsilite and low-nepheline, below approximately 1000°C. The composition of the coexisting phases in the miscibility gap has been measured by X-ray methods. One of the most interesting features of this unmixing was the rapidity of the process. For example, when a single phase quenched from a high temperature was heated in an X-ray

camera at 500°C, unmixing began within five minutes. Accordingly, measurements on the top of the miscibility gap are uncertain, for some unmixing may have occurred during quenching.

It is not surprising that kalsilite is the common modification of $KAlSiO_4$ found in the volcanic rocks, for this is the stable form in the temperature range expected in these rocks. The inversion temperature of kalsilite at atmospheric pressure is 840°C in pure $KAlSiO_4$ and rises rapidly with increasing solid solution of $NaAlSiO_4$. Kaliophilite, found in ejected blocks at Monte Somma,

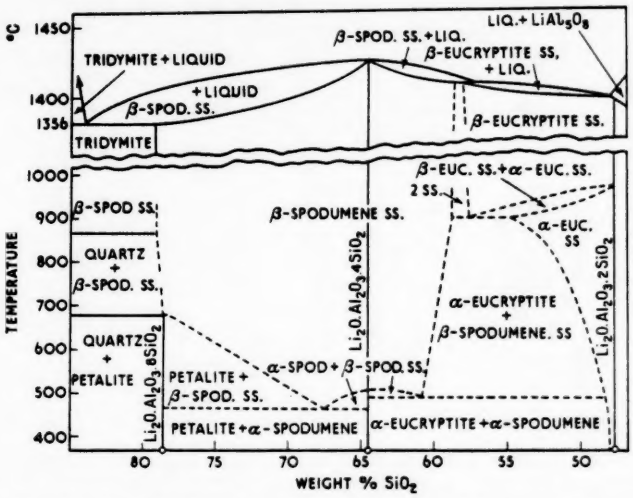

Fig. 20. Results of a hydrothermal study of a system involving no water-containing phases. The system Li_2O—$Al_2O_3 \cdot 2SiO_2$—SiO_2 after Roy, Roy and Osborn. The water here serves only as a "mineralizer" making it possible to obtain relationships which could not be studied in the "dry" way.

Vesuvius, is apparently different from all the synthetic phases encountered in this study.

An inversion has been found in low-nepheline of composition 100 per cent $NaAlSiO_4$ at 850°C, for material crystallized dry at 1150°C. Below this temperature it is hexagonal, and above it the symmetry is lowered to orthorhombic. The inversion is rapid and of the displacive type. A small heat effect was observed at 850°C, on the differential thermal analysis apparatus. Low-nepheline made hydrothermally at 800°C also shows this inversion, but at the higher temperature of approximately 1000°C. Its lattice parameters are also slightly different at room temperature, but the reason for this discrepancy has not yet been established. No inversion has so far been found in low-nepheline of adjacent compositions.

Lattice parameters have been determined for the nepheline-kalsilite solid solutions as a function of composition. The results have proved useful in estimating the composition of natural nepheline-kalsilite solid solutions. The presence of excess silica (albite) in solid solution apparently does not greatly influence the determination of the ratio of $KAlSiO_4$ to $NaAlSiO_4$.

Another interesting result of the study is the sharp change of slope in the lattice

parameters *a* and *c* of low-nepheline when plotted against alkali ratio at room temperature. This discontinuity is at a ratio corresponding to three sodium atoms and one potassium atom. There is also a break between 90 per cent and 100 per cent $NaAlSiO_4$, presumably related to the inversion in pure $NaAlSiO_4$.

Almandine Stability

YODER (1955) has studied the stability of almandine as a function of temperature and pressure. The data illustrated in Fig. 21 show that almandine decomposes

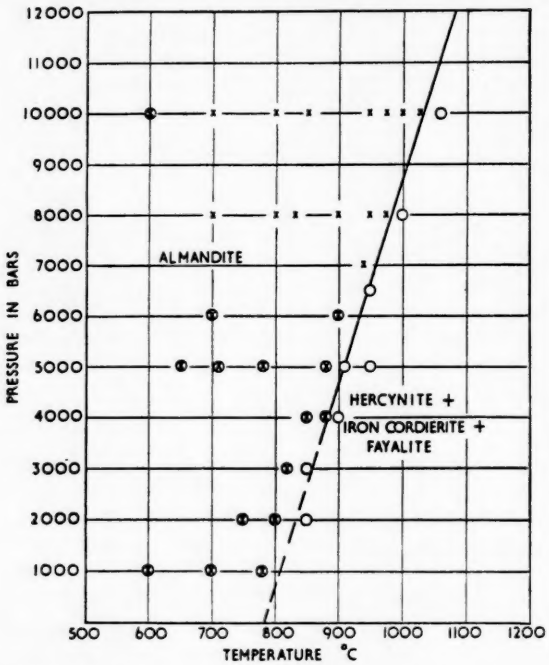

Fig. 21. *p–t* curve for the reaction: almandine $\rightleftarrows$ hercynite + iron cordierite + fayalite, after YODER.

at higher temperatures into hercynite + iron-cordierite + fayalite, the *p–t* curve for the reaction has been determined. Some data on the almandine-spessartite series have been obtained by M. MICHEL-LEVY (1951).

Chlorite Relationships

NELSON and ROY (1954, loc. cit.) established experimentally the existence of a dimorphic series of solid solutions extending from amesite ($Mg_4Al_2 \cdot Si_2Al_2 \cdot O_{10}(OH)_4$) to at least as far as penninite. They were able to establish this for both synthetic and naturally occurring samples—thus unifying the picture of the chlorite compositions. Maximum stability at 1000 kg/cm^2 appears near the clinochlore composition which is stable to about 700°C, a value which decreases towards both amesite and penninite. Cr-substituted chlorites kaemmererite and kotschubeite and synthetic analogues have been studied by DEVRIES and ROY (1954, unpublished). The amount of Cr-substitution appears to be limited to a maxi-

mum of half the total of (Cr + Al); both 7 Å and 14 Å polymorphs are found and their general *p–t* relations are very similar to the pure Al members, higher pressure and temperatures favouring the 14 Å polymorph. The decomposition temperatures are lowered 50 to 100°C when compared to the pure Al members.

LACY (1951b) has studied "artificial" metamorphism of some natural rocks and obtains a maximum stability of 650°C for a natural chlorite. He has designed and used an interesting vessel combining some of the advantages of the Morey bomb and the cold-seal apparatus (1951a).

$(Mg{\cdot}Ni{\cdot}Zn)O—(Si{\cdot}Ge)O_2—H_2O$

ROY and ROY (1954, loc. cit.) have presented some data on these systems including a set of tentative triangles describing the stable phase assemblages in the systems $NiO—SiO_2—H_2O$ and $MgO—GeO_2—H_2O$. The comparison of the decomposition temperatures of the layer silicates in these systems with the Mg—Si analogues shows some surprising features such as the greater stability of the Ni—Si serpentine. The olivine-spinel transformation has been confirmed for Mg_2GeO_4 and a fairly precise volume change measured; current *p–t–x* studies of the system $Mg_2SiO_4—Mg_2GeO_4$ promise to yield data of significance in seismic interpretations.

$CaSO_4—H_2O$

Among the several recent investigations of this system the most interesting is that by MACDONALD (1953) who has studied the gypsum-anhydrite relationships both for fresh and "salt-water" conditions, by correlating thermochemical data with experimental and geological data. The variation of the equilibrium temperature of 40°C (1 atm. and "pure" water) with pressure and salinity has been calculated for the reaction:

$$\underset{\text{(gypsum)}}{CaSO_4{\cdot}2H_2O} \leftrightharpoons \underset{\text{(anhydrite)}}{CaSO_4} + 2H_2O.$$

Carbonate Systems

Although not strictly "hydrothermal", studies involving CO_2 as the significant volatile are closely related to the subject under review. Most of the current interest concerns the calcite-magnesite-dolomite problems.

MILLER (1952) studied the system $CaCO_3—H_2O$ in the presence of CO_2 under pressure, arriving at slightly different solubility values than earlier workers. The solubility was also measured in the presence of NaCl solutions of varying strength.

Laboratory studies on the thermal dissociation of calcite, dolomite and magnesite have been in progress for several decades but the majority of the work has been done by differential thermal analysis and at relatively low pressures. SMYTH and ADAMS, however, as early as 1923 (loc. cit.) studied dissociation and melting in the system $CaO—CO_2$ by differential thermal analysis and worked up to pressures of over 1000 kg/cm².

HARKER and TUTTLE (1955) studying the system $CaO—MgO—SiO_2—CO_2$ have determined the *p–t* curve for the thermal dissociation of calcite using the cold-seal quenching apparatus and, by this means, found the calcite *p–t* curve to be somewhat lower than that determined by SMYTH and ADAMS. Using the same quenching apparatus, HARKER and TUTTLE determined the corresponding

p–t curves for magnesite and dolomite which are illustrated in Fig. 22. They also investigated the limits of solid solution between 500 and 900°C along the binary join $CaCO_3$—$MgCO_3$ with the results shown in Fig. 23. Similar data have been obtained by GOLDSMITH and GRAF (1954) for the dolomite decomposition.

These data are of importance not only because of the common occurrence of limestones and dolomites but also because Ca—Mg carbonate minerals assume a major role in certain controversial rock types of igneous complexes.

SCHLOEMER (1952, 1954) has studied several reactions involving two volatiles

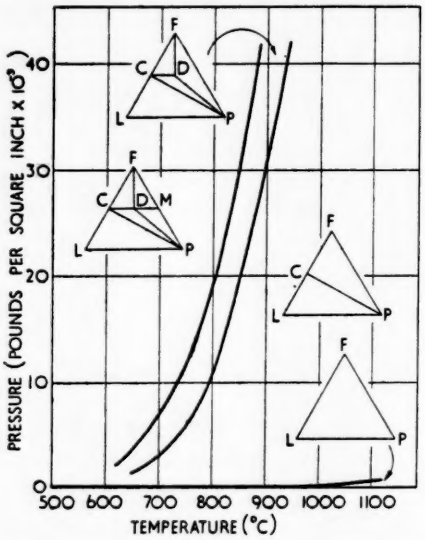

Fig. 22. Univariant pressure (CO_2)-temperature curves for the dissociation of calcite dolomite and magnesite. The triangular diagrams indicate the phases which would be stable in the divariant regions defined by the *p–t* curves ignoring any solid solution. F = CO_2, C = Calcite, D = Dolomite, M = Magnesite, L = lime, P = periclase, after HARKER and TUTTLE.

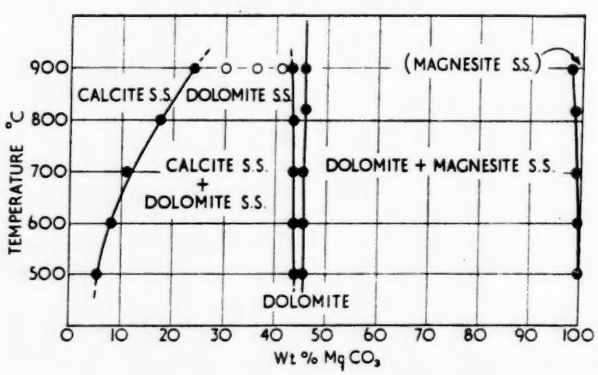

Fig. 23. Limits of solid solution in the system $CaCO_3$—$MgCO_3$ between 500 and 900°C, after HARKER and TUTTLE.

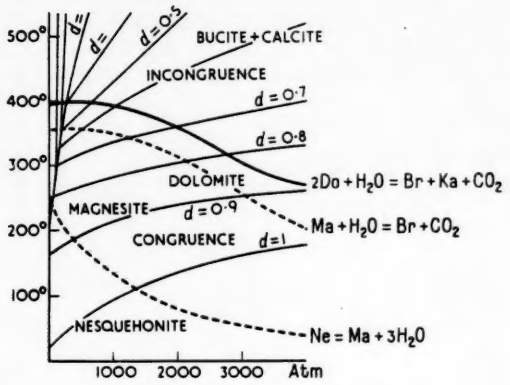

Fig. 24. *p–t* curves for certain reactions in the system CaO—MgO—CO_2—H_2O after SCHLOEMER. Pressure is water pressure. The curve for nesquehonite decomposition is almost certainly incorrect.

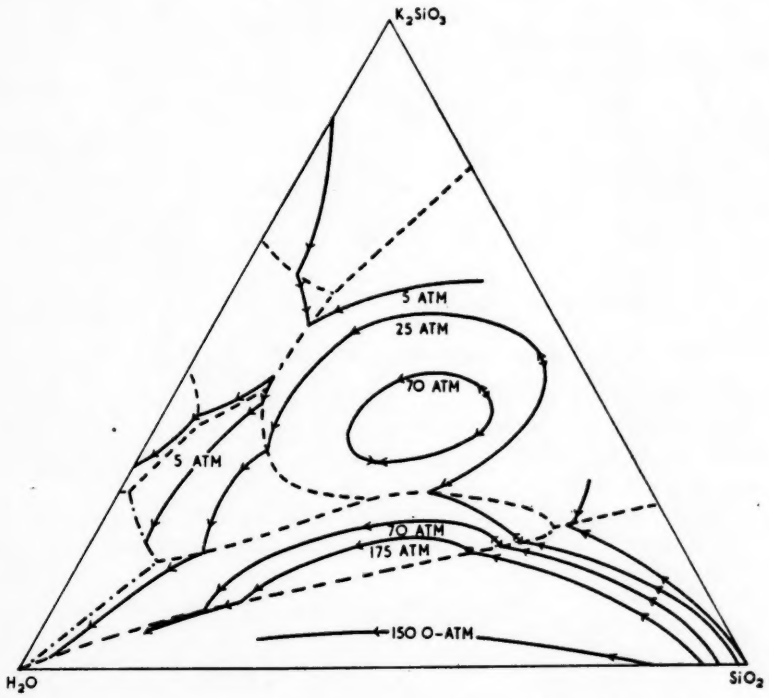

Fig. 25. Isothermal saturation diagram for the system K_2SiO_3—SiO_2—H_2O after MOREY. A solid *p–x* model has been reproduced in the original paper. This section has been revised by MOREY (Commentary on the Scientific Writings of J. WILLARD GIBBS, Vol. 1, p. 270).

in the system CaO—MgO—CO_2—H_2O as a function of temperature and pressure of one volatile (water). Besides providing data on certain dehydration reactions such data can be of use in explaining the phenomena associated with dedolomitization: Fig. 24 represents a summary of much of this work.

Theoretical Advances

A few papers have appeared recently dealing with the general problem of the *p–t–x* relations in systems involving critical phenomena of relatively concentrated solutions.

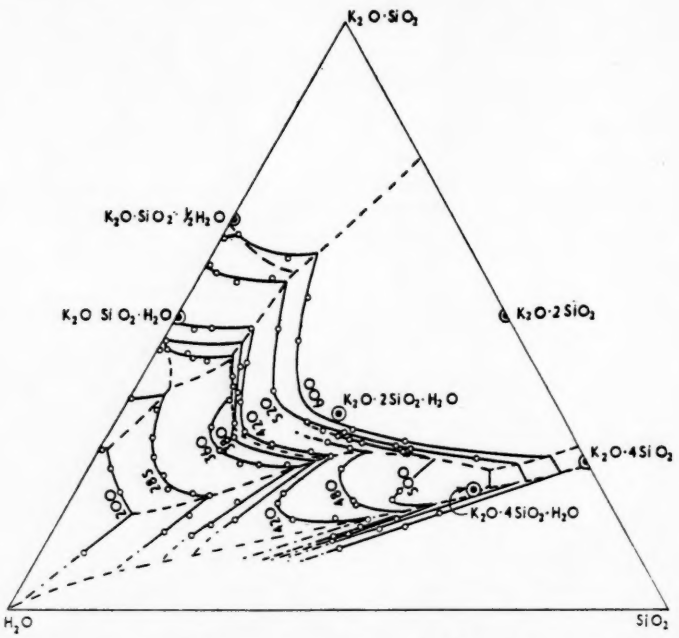

Fig. 26. Isobaric saturation diagram for the system K_2SiO_3—SiO_2—H_2O, after MOREY.

MOREY (1953) has studied in detail the system NaCl—H_2O as an example of such a system illustrating the nature of the phase surfaces, and the realization of the second critical endpoints. He has also discussed such systems in a general treatment of the problem.

I. A. OSTROVSKY (1950, 1953) has treated more specificially the case of the *p–t–x* diagram of a silicate melt in equilibrium with concentrated solutions in the supercritical region.

LIQUIDUS STUDIES

The earliest systematic hydrothermal liquidus studies were carried out by MOREY and FENNER (1917, loc. cit.). This work has already been mentioned. Results of this study can be summarized in two figures which illustrate the isothermal and isobaric saturation curves for the system K_2SiO_3—SiO_2—H_2O (Figs. 25 and 26). These *t–x* and *p–x* sections give the temperatures and pressures at which liquids of known composition are in equilibrium with the various

crystalline phases and a vapour phase. Altogether eight crystalline phases appear at the liquidus in this system. Four new crystalline phases were discovered during this systematic study as a by-product of the equilibrium studies. The next paper dealing with liquidus determinations was by GORANSON (1938, loc. cit.) on the systems albite-water and orthoclase-water. This work represents an important step forward because the common rock-forming silicates were studied. The effect of water vapour under pressure is remarkable; the liquidus of albite, for example, is lowered 300°C at 3000 kg/cm² (Fig. 27) water vapour pressure and the incongruent melting relation of orthoclase is completely removed at a water

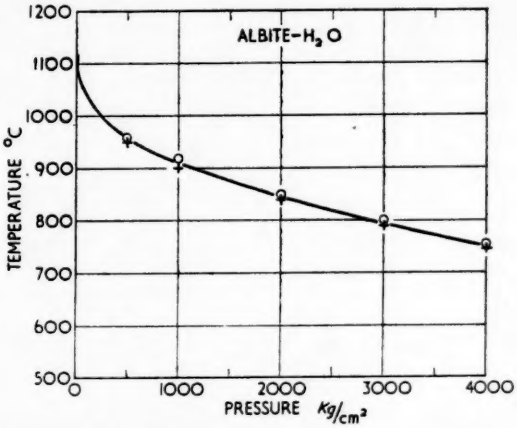

Fig. 27. The lowering of the liquidus temperature of albite as a function of water pressure, after GORANSON.

vapour pressure of about 2600 kg/cm². Perhaps the most important feature of this study was the conclusive evidence presented showing that the critical curve must intersect the liquidus and give rise to a critical end point lying at pressures in excess of 4000 kg/cm² and perhaps at pressures in excess of those present in the earth's crust. In other words, it is unlikely that liquids having these anhydrous compositions would ever carry more than about 10 per cent water in solution in the outer 15 km of the earth's crust.

The next reported liquidus study in which a rock forming silicate was an important phase was by TUTTLE and FRIEDMAN (1948) and FRIEDMAN (1950, loc. cit.). They studied a portion of the system H_2O—Na_2O—SiO_2 at 250, 300, 350, 400 and 450°C. The most interesting feature of this system is the region of liquid immiscibility bordering the quartz stability field. Apparently the immiscibility disappears at lower temperatures (i.e. < 225°C) and one liquid appears to change composition in such a fashion that at a temperature slightly above 375°C the critical surface is intersected and at higher temperatures only one liquid coexists with a vapour having essentially the same composition as the liquid at 375°C. One isothermal section (350°C) is shown in Fig. 28. Like the H_2O—K_2O—SiO_2 system studied by MOREY and FENNER (1917, loc. cit.) the system H_2O—Na_2O—SiO_2 illustrates the relationship that there can be complete solubility between anhydrous silicate compositions and water.

A portion of the system K_2O—Al_2O_3—SiO_2—H_2O was studied by TUTTLE

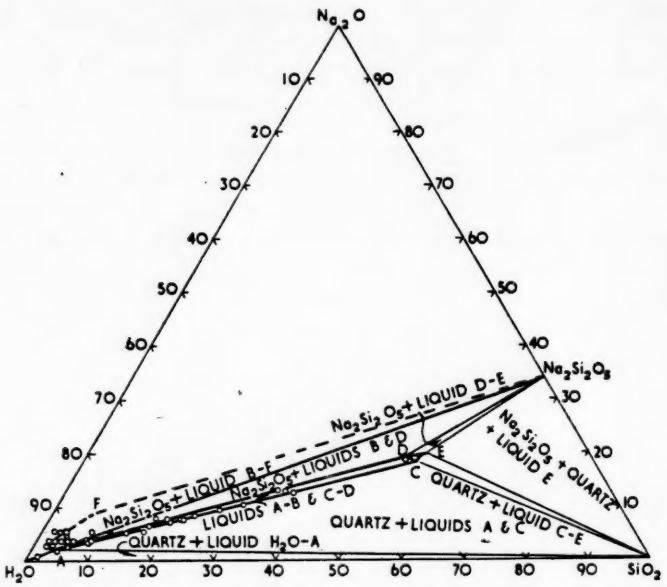

Fig. 28. Isothermal section in the system Na_2O—SiO_2—H_2O at 350°C, after TUTTLE AND FRIEDMAN

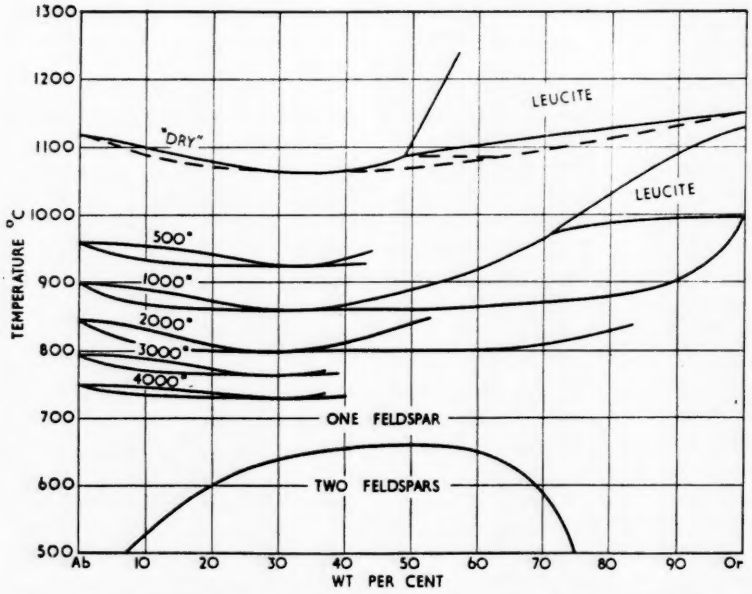

Fig. 29. The change in liquidus relationships in the system albite-orthoclase as a function of water pressure, after TUTTLE and BOWEN.

(1948, loc. cit.) at the liquidus and here the effect of water on the liquidus is indeed remarkable in the alkali rich section of the potassium disilicate-leucite join; the liquidus is lowered over 400°C by 1000 kg/cm² water vapour pressure. Here too the indications are that a complete solubility relation exists between anhydrous silicates and water.

Liquidus relations in the system $NaAlSi_3O_8$—$KAlSi_3O_8$—H_2O have been studied by BOWEN and TUTTLE (1950) at several pressures of water (Fig. 29).

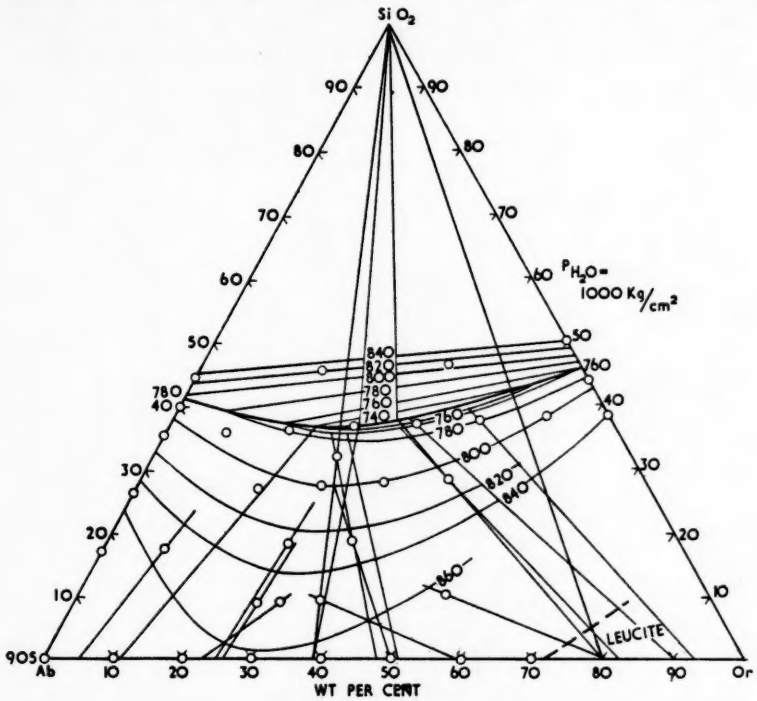

Fig. 30. Isobaric section showing equilibrium relations in the system albite-quartz-orthoclase-water, after BOWEN and TUTTLE.

Here for the first time liquidus determinations have been made on compositions closely approaching the natural rocks—the trachytes. The general nature of the "dry" liquidus remains unchanged and the principal effect of water vapour is to lower the liquidus temperatures. Water has an outstanding effect on one equilibrium, and that is on the incongruent melting of $KAlSi_3O_8$. At a pressure of about 2700 kg/cm² the $KAlSi_3O_8$ composition melts directly to a hydrous liquid without the appearance of leucite, and at higher pressures of water vapour the system is ternary. Perhaps the outstanding feature of this study was the evidence found to support the indications long since found in the rocks that a complete series of solid solutions exists between $KAlSi_3O_8$ and $NaAlSi_3O_8$ at elevated temperatures.

The system $NaAlSi_3O_8$—$KAlSi_3O_8$—SiO_2—H_2O has been studied at pressures of water vapour up to 4000 kg/cm² (TUTTLE and BOWEN, 1952). The results of

the liquidus studies can be shown on a ternary diagram by projecting the temperatures (isotherms) or pressures (isobars) onto the anhydrous base of the tetrahedron. Such a projection for a water vapour pressure of 1000 kg/cm² is illustrated in Fig. 30. The principal feature of the diagram is the pronounced trough near the centre toward which all liquids move on crystallization. This thermal sink is the Rome toward which all crystallization roads in the system lead. On fractional crystallization all liquids change their composition in such a fashion that they will reach, or nearly reach, this isobaric ternary minimum. It is, therefore, expected that the rocks high in these constituents (the granites) will have their compositions controlled by this isobaric minimum if they have

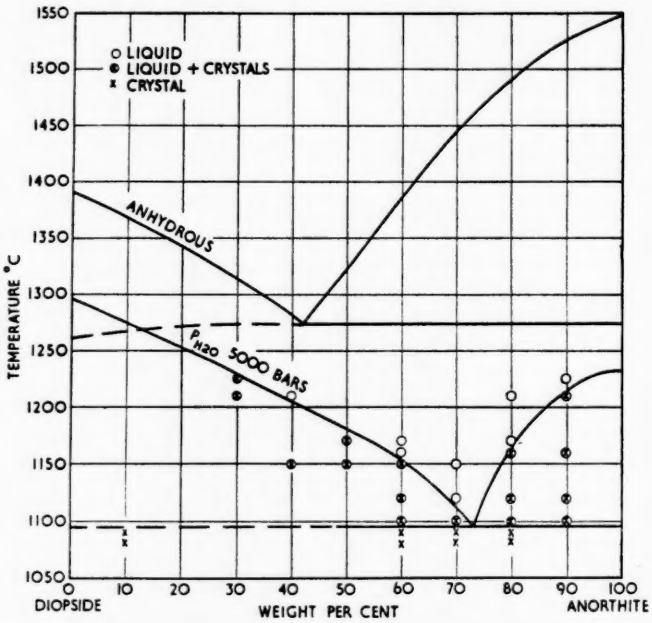

Fig. 31. The influence of water pressure on equilibrium relations in the system diopside-anorthite, after YODER.

gone through a liquid stage, either by remelting or by fractional crystallization of more basic liquids. The fact that granites do have compositions grouped near this minimum strongly supports the magmatic theories for the origin of granite.

The silica-rich portion of the SiO_2—H_2O system has been studied by TUTTLE and ENGLAND (1955) and it was found that the liquidus of cristobalite is lowered rapidly by water vapour under pressure. The first 1000 kg/cm² water vapour pressure lowers the liquidus nearly two and one half times the amount of lowering produced in albite composition by a comparable pressure.

YODER (1952, loc. cit.) determined the change of melting point of diopside as a function of argon pressure, and later YODER (personal communication) has studied the lowering of the liquidus in the system diopside—anorthite—water at 5000 kg/cm² water pressure and as seen in Fig. 31, a most significant change in the position of the eutectic towards the anorthite composition takes place,

consequent upon the lowering of the anorthite melting point by almost 325°C. The diopside melting point is hardly changed 100°C at the same pressure.

This remarkable lowering of the anorthite liquidus indicates that a considerable amount of water is dissolving in anorthite liquid. This has an important bearing on the solubility of water in basaltic liquids. In general it has been thought that water was much less soluble in basaltic than in granitic liquids. These results appear to indicate that water is indeed very soluble in basaltic liquids and it is expected that this will introduce a multitude of possibilities into the various courses of crystallization of basaltic liquids during equilibrium and fractional crystallization.

SUMMARY

Four types of information are obtained from subsolidus studies in hydrothermal systems which have applications to geological problems: (1) pressures and temperatures of the breakdown of compounds containing a volatile component, e.g. $Al(OH)_3$; $KAl_2 \cdot AlSi_3O_{10}(OH)_2$; $MgCO_3$; or pressures and temperatures of reactions, e.g. serpentine + brucite $\leftrightharpoons$ forsterite + vapour; (2) pressure and temperature of polymorphic transitions (not a hydrothermal reaction strictly speaking, but as a volatile material is commonly necessary to promote the transition such inversions are included here e.g. the quartz-tridymite inversion); (3) the change in the extent of solid solution as a function of temperature and pressure (the effect of pressure is usually relatively small compared with the temperature effect and in cases such as the feldspar solvus, pressures can be disregarded for most purposes), e.g. solid solution of magnesite in calcite or of orthoclase in albite; (4) the pressure and temperature requirements for the stable coexistence of any assemblage of minerals.

This information on the physical chemistry of the earth can be applied in different areas. Each of the above types of information can, for instance, be used in geothermometry in the broadest sense of the term. Much of the information can be used directly in problems concerning the origin of rock types; thus the studies on the stability of serpentine have shown that this mineral will decompose at temperatures far below those required by the theories which demand magmas of this composition to account for the origin of many serpentine masses. The information can be used to select assemblages which may be used to characterize metamorphic facies.

One of the outstanding results of these crystal-vapour equilibrium studies has been the unexpectedly high temperature range of stability of some minerals and mineral assemblages which from field studies had been thought to be very much lower. For example, chlorite, talc and muscovite, which appear at the greenschist level in metamorphism are stable up to magmatic temperatures (i.e. 600°C at 2000 kg/cm^2 H_2O). Hence, it is possible to have sanidine and chlorite or sanidine and talc coexisting in stable equilibrium at temperatures high enough to result in actual fusion of the lowest melting fraction of the rocks if the composition is appropriate. This is not to advocate that the temperatures were actually this high, but it should be kept in mind that such temperatures are possible if the water vapour pressure remains high during metamorphism. And so it is with all the other higher grade facies—the diagnostic minerals are apparently stable at magmatic temperatures when the water vapour pressure is appreciable.

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As mentioned in the historical review, another important geological concept to evolve from hydrothermal studies was the relation between pressure, temperature and composition in silicate-water systems. MOREY (1922, loc. cit.) pointed out that very high pressures could be expected as a result of crystallization in systems containing volatile components. GORANSON's (1931, loc. cit.) later work on granite-water mixtures proved conclusively that the pressures so generated could well exceed those required as a possible source for volcanic explosions. Also, in addition to the initial explosive eruption crystallization can cause successive explosions by alternate relief of the pressure followed by further crystallization.

A second important feature of silicate-water systems discovered in the early studies of MOREY was the fact that all compositions between water and anhydrous silicate melts were possible in compositions containing alkalies. This information can be extrapolated to granite compositions and thus affords a reasonable mechanism for producing the large zoned pegmatites associated with granitic rocks as well as a source of hydrothermal solutions which carry the ores and give rise to granitization in the wall rocks of batholiths. The studies of GORANSON on granite-water mixtures appear to contradict the above concept as he has shown that only a limited amount of water will dissolve in a granite liquid at pressures expected in the earth's crust. However, the mixtures he used did not contain an excess of alkalies as granites and rhyolites commonly do, and therefore, his results cannot be used to prove that continuous solubility is impossible and that the early theories are incorrect.

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THE GEOCHEMISTRY OF THE HALOGENS

by CARL W. CORRENS

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INTRODUCTION

BY far the greatest part of geochemical work is concerned with cations. It therefore seems desirable, for once in a way, to consider the behaviour of anions; and to this end, shortly before the second World War, we started investigations in Göttingen of the behaviour of fluorine. Because of the war and its aftermath, this work on fluorine—which was begun by S. KORITNIG with the development of a reliable method for its determination—first appeared in 1951. In addition, chlorine and bromine were investigated by BEHNE (1953). Meanwhile, in 1940, the work of SHEPHERD on fluorine and the work of SELIVANOV on chlorine and bromine appeared. In 1945 and 1947 BARTH published works on fluorine, while in 1953 the paper by KURODA and SANDELL on chlorine appeared. Through the courtesy of Dr. L. H. AHRENS I have also been able to make use of an unpublished doctorate thesis by SERAPHIM, which was completed in 1951 and which contains many spectrographic determinations of fluorine. In the case of iodine, however, most of the work dates from rather far back, especially the important contributions of v. FELLENBERG (1924–1927).

On the basis of these new investigations, it appears an attractive proposition

[Translated from the original German by Dr. E. A. VINCENT, Department of Geology and Mineralogy, Oxford.]

to try and gather together the geochemistry of the halogens, the much more so since the two text books of geochemistry, that of RANKAMA and SAHAMA, which appeared in 1950, and the posthumous work of GOLDSCHMIDT (1954) essentially base their discussion upon the older data. As well as including the data contained in the works already quoted, I have also been careful to add further newer data to be found in the literature, and to amplify these, where necessary, by drawing again upon the older results, so that the following summary may serve as an amplification of the text books. Since, in my opinion, the material which is available is still too fragmentary for a proper statistical treatment, I have attempted, as far as is possible, to refer to such examples in which both rocks and constituent minerals are well known in order to indicate the possibilities of the geochemical behaviour of the halogens.

The following pages deal only with the four halogens already mentioned; the element astatine, which is only known in radioactive isotopes of very short life, can merely be mentioned here.

I. COSMOS AND METEORITES

The following table taken from UREY (1952) gives information about the cosmic abundance of the halogens:

Table 1. Atomic Abundance of Halogens : 10,000 Si (*after* UREY)

	V. M. GOLDSCHMIDT	HARRISON BROWN	UREY
F	15	90	3
Cl	40–60	170	21
Br	0·43	0·42	0·49
I	0·014	0·018	0·015

As can be seen, the values given by different authors for fluorine and chlorine vary considerably. All these authorities are in agreement, however, that the cosmic abundance of chlorine is greater than that of fluorine, while in the crust of the earth fluorine is more abundant than chlorine. Further research is clearly necessary.

There are several new works dealing with the abundance of halogens in meteorites, but unfortunately not with fluorine. For this element there are only the older data of GOLDSCHMIDT (1938), who gives 28 ppm F. I. and W. NODDACK state that in the meteorites the ratio of the atomic abundance F:Si = 3:10,000.

For chlorine and bromine there are several new determinations by BEHNE, and for chlorine alone spectrographic determinations on 20 stony meteorites by E. SALPETER (1952). Older determinations of bromine and iodine were given by VON FELLENBERG. These figures are collected together in Table 2. SALPETER's values are usually significantly higher than those of BEHNE. In the Admire meteorite, SALPETER found 6400 ppm Cl; in the 19 remaining cases the values varied between 100 ppm (Bluff and Dalat) and 2050 (Lancé). The mean value for these 19 meteorites, as well as the analyses by BEHNE, and by VON FELLENBERG and LUNDE, for Br and I, are given in Table 2. Since these

two investigations were not of the same meteorites, an exchange of material between the authors has been arranged. In the older literature there are some

Table 2. Halogen Contents of Meteorites, in ppm

		Cl	Br	I	Authority
Irons	Braunau	≦ 20	≦ 1		BEHNE
	Arispe	80			BEHNE
	Charlotte	≦ 20			BEHNE
	Toluca		5	1·50	V. FELLENBERG and LUNDE, 1927
	Toluca, oxidized crust	340	6·6		BEHNE; V. FELLENBERG and LUNDE, 1927
	Canon Diablo, oxidized crust	≦ 60	2	0·48	BEHNE; V. FELLENBERG and LUNDE, 1927
Iron-Silicate	Bomba, iron		24	0·15	V. FELLENBERG and LUNDE, 1927
	Bomba, silicate		18	1·05	V. FELLENBERG and LUNDE, 1927
Stones	Mocs		20	1·80	V. FELLENBERG and LUNDE, 1927
		110	11·4		BEHNE
	Stannern	≦ 20	5		BEHNE
	Chateau Renard	100			BEHNE
	Ergheo, troilite and Fe-portion		20	0·70	V. FELLENBERG and LUNDE, 1927
	Ergheo, silicate portion		56	1·24	V. FELLENBERG and LUNDE, 1927
	Admire	6,400			SALPETER
	Mean of 19	824			SALPETER
	Average	300			MERRILL, 1930

values which are even higher than those of SALPETER. There is also a mineral, lawrencite, $FeCl_2$, which has been described from meteorites, and which was also found in the iron of Ovifak, Greenland (DANA), in the analysis of which (CLARKE) 200 and 800 ppm Cl were reported. A clarification of the question of the chlorine content of meteorites appears to be urgently needed.

II. MAGMATIC ROCKS

Although the whole concept of a magmatic origin for certain rocks—especially for the acid plutonic rocks—is nowadays hotly debated, we shall adhere to it for the following discussion, because a firm distinction of the data available in the literature which refer to true magmatic rocks and to rocks which are more or less similar, but which may have different origins, is not possible.

If we examine (Table 3) data for the plutonic rocks, we shall see that for none of the halogens is there any significant relationship between halogen content

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Table 3. Halogen Contents of Plutonic Rocks, in ppm

	F	Cl	Br	I	P_2O_5	Authority and remarks
Granite, Stone Mt., Georgia	390	300				SHEPHERD
Granite, Petrick Llano Region, Texas	1,200	300			1,400	F and P_2O_5: GOLDICH, 1941. Cl: KURODA and SANDELL Granite contains fluorite
Granite, Schierke, Harz	860	270	1·2		500	KORITNIG, BEHNE
Hornblende-granite, Teufelsberg, Odenwald		300	2		2,200	Cl: BEHNE; P_2O_5: P. SCHNEIDERHÖHN
13 German granites	1,330	80	1		1,570	KORITNIG, BEHNE
3 Biotite-granites, Norway Mean:	400–1,000 630	400	(2)	(0·2)	700	BARTH, 1945, 1947 Br, I: v. FELLENBERG and LUNDE, 1927
Mica-granites, New England Mean:	220–2,700 730					SERAPHIM
26 Granites, various localities in U.S.A. Mean:	20–2,300 830	(220)				F: SERAPHIM Cl: 99 Granites—KURODA and SANDELL
Standard mixture, East Fennoscandian rapakivi granites	3,600	600			1,800	SAHAMA, 1948
Muscovite-bearing microcline granite Finland	300	400			3,000	SIMONEN
Granodiorite, Aulanko area, Finland	200	800			1,300	SIMONEN
Granodiorite (Opdalit) Ulsberg, Norway	660	20	7·4		2,540	KORITNIG, BEHNE
Quartz-diorite (Tonalite) Adamello, Italy	340	100	3·4		800	KORITNIG, BEHNE
Diorite, Reichenbach, Odenwald		240	3·7		2,000	Cl: BEHNE, P_2O_5: P. SCHNEIDERHÖHN
Quartz-diorite, Aulanko area, Finland	300	700			3,000	SIMONEN
5 Quartzdiorites and Diorites	670	(350)				F: SERAPHIM Cl: 4 Diorites, Oregon KURODA and SANDELL
3 Diorites, California		450				KURODA and SANDELL
22 Nepheline syenites (v. ENGELHARDT)	1,190	970	3		2,660	KORITNIG, BEHNE
Syenite, Zitschewig, Dresden	1,060	450	2·6		2,190	KORITNIG, BEHNE

Table 3 (contd.)—

	F	Cl	Br	I	P_2O_5	Authority and remarks
5 Nordmarkitic Alkali syenites, Norway Mean:	500–1,100 860	200			2,000	BARTH, 1945, 1947
4 Larvikites, Norway	780	670		(0·3)	5,900	F, Cl, P_2O_5: BARTH, 1945, 1947 I: v. FELLENBERG and LUNDE, 1926
16 Syenites and feldspathoidal syenites Mean:	200–4,000 1,480	(550)				SERAPHIM: F KURODA and SANDELL: Cl in 6 Syenites, N.Y. and Minn.
20 Gabbros		210				KURODA and SANDELL
11 Gabbros (Noll)	310	80	3·8		210	KORITNIG, BEHNE
2 Oslo Essexites	700	650				BARTH, 1945, 1947
Dunite (feldspathic), Lewis Hills, Newfoundland		1,000				KURODA and SANDELL
10 Ultramafic rocks		340				KURODA and SANDELL

Note: (v. ENGELHARDT) (NOLL), indicate average mixtures from V. M. GOLDSCHMIDT's institute, prepared by and first utilized by these authors. (Figures in brackets refer to rocks of the same type, but from a different locality.)

and content of SiO_2. Admittedly, the analyses of gabbros show lower values of chlorine and fluorine than the granites, but the essexites show higher values again. The limited number of analyses for bromine and iodine does not allow us to postulate any definite rule for these elements.

In Table 4, figures for the halogen contents of effusive and hypabyssal rocks are presented. The astonishingly high F content of many basalts is to be noted. Basalts of the Hoher Hagen and of Bramburg in the neighbourhood of Göttingen, which have been investigated petrographically by WEDEPOHL and which are very similar in composition, outcrop only 15 km away from one another, yet are nevertheless distinguishable not only in F content but also in Cl and Br, far beyond the possible limits of experimental error. In all the analyses in Tables 3 and 4 it is clearly seen how great the variations of these elements within rocks of similar type may be. They show, moreover, that the variations, at least in the cases of F, Cl and Br, lie well outside the limits of error. It is also evident that different authors are in agreement over orders of magnitude. Because of the wide variations within similar rocks, I have not ventured to deal only with averages. I cannot agree either with SIMONEN, who in 1948 attempted to show, on the basis of diagrams prepared from older analyses, that basic rocks are richer in chlorine, while acid rocks are richer in fluorine. His own values vary widely in the case of chlorine, while in the case of fluorine there are too few analyses. In addition, the similar idea that plutonic rocks have higher halogen content than effusive rocks, because the halogens can be incorporated

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Table 4. Halogen contents of Effusive and Hypabyssal Rocks, in ppm

	F	Cl	Br	I	P_2O_5	Authority and remarks
Aplite, Petrick Llano region, Texas, fluorite-bearing	1,300	150			600	Contains fluorite
Llanit (granite porphyry), Babyhead, Llano region, Texas, fluorite-bearing	2,500	170			tr	F and P_2O_5: GOLDICH, 1941 Cl: KURODA and SANDELL
Liparite, Eisenbach, Hungary	750	20	4		330	KORITNIG and BEHNE
Trachyte, Drachenfels	830	20	4·7		1,400	KORITNIG and BEHNE
14 Andesites, Methana, v. ENGELHARDT	390				1,290	KORITNIG
6 Andesites, Ägina, v. ENGELHARDT	620				1,170	KORITNIG
Amphibole-andesite, Stenzelberg, Siebengebirge		200	2		2,900	Cl: BEHNE P_2O_5: P. SCHNEIDERHÖHN
Augite-andesite, Tokaj, Hungary		110	5·8			BEHNE
Uralite-porphyrite, Aulanko area, Finland	100	300			6,600	SIMONEN
Plagioclase-porphyrite, Aulanko area, Finland	200	300			7,300	SIMONEN
Intermediate volcanic rock, Aulanko area, Finland	200	200			2,900	SIMONEN
Trachyandesite, Sabinyo, Uganda	600	100			4,000	TURNER and VERHOOGEN
10 Bohemian Phonolithes, v. ENGELHARDT	270	160	1		1,500	KORITNIG and BEHNE
Nepheline-phonolithe, Kletschnerberg		20	2·5			BEHNE
Oligoclase-andesine-basalt (Mugearite) New Zealand	500	1,100			15,000	TURNER and VERHOOGEN
Basalt, Hoher Hagen	270	30	7·3		3,600	KORITNIG and BEHNE
Basalt, Bramburg	800	120	2·2		684	KORITNIG and BEHNE
Basalt, Mt. Morrison, California	1,060	100				SHEPHERD
Porphyritic feldspar basalt, Masafuera, Juan Fernandez Island	1,500	800			4,600	QUENSEL, 1952
Feldspar basalt, Dattenberg bei Linz a. Rhein			8	0·31		v. FELLENBERG and LUNDE, 1926
16 Basalts, Columbia Plateau Mean:	150–800 540					SERAPHIM
5 Basalts, Iceland	180				1,920	BARTH, 1947

Table 4 (contd.)—

	F	Cl	Br	I	P_2O_5	Authority and remarks
Diabase, effusive, N.W. Kiruna	500	1,000			700	LARSSON, No. 315
Olivine Diabase, W. of Hannberget, N. Ulfon	1,900	600			4,200	LARSSON, No. 341
Mauna Loa, 1926 flow, Hawaii	90	100				SHEPHERD
New Core, No. 6 Spine, 1902, Mt. Pelée, Martinique	80	200				SHEPHERD
Melilite-basalt, Hofgeismar	1,100				10,200	F: KORITNIG P_2O_5: Th. ERNST
Leucite-basalt (Ugandi), Muzanza Lencite-basalt (Ugandite), Uganda	500	500			6,200	TURNER and VERHOOGEN after HOLMES
Lutalite, Lutale, Uganda	1,100	1,100			9,000	TURNER and VERHOOGEN after HOLMES.
Mikenite, Mikeno, Uganda	800	1,400			7,700	TURNER and VERHOOGEN after HOLMES
Leucite-basanite, Kivit, Busamba, Uganda	900	1,000			7,400	TURNER and VERHOOGEN after HOLMES
Leucite-basanite (Murambite), Murambe, Uganda	700	100			5,500	TURNER and VERHOOGEN after HOLMES
Limburgite, dyke, Kawerau gorge, New Zealand	1,500	200			16,500	TURNER and VERHOOGEN after BENSON
Kimberlite, Kimberley	450	140			16,400	F: SERAPHIM P_2O_5: TRÖGER Cl: KURODA and SANDELL

into the crystal lattices of minerals under plutonic conditions of crystallization, cannot be confirmed by the quantitative data available. We may state that in all probability the halogen content of a rock does not depend solely upon its mineralogical composition and mode of crystallization, but also upon the halogens which were available in the original melt. In order to examine these questions, we must next examine how the halogens actually occur in rocks.

1. We may have minerals in which the halogens are built into the lattice as regular constituents, i.e. halogen minerals. Of the minerals rich in fluorine, only fluorite has been observed in granites and acid hypabyssal rocks—as, for example, in the granite of Schierke, Harz; of the Petrick Llano region in Texas, and in the aplite of the same locality. It seems to me very doubtful whether we are dealing here with "magmatic crystallization"; I would rather believe that the fluorite is of secondary formation connected with loss of volatiles from the magma, and thus properly belonging to the stage of greisen

formation. Fluorite contains 51·33 per cent F, and so can cause quite a high fluorine content in a rock even when the mineral is present in small quantity. Furthermore, fluorite, as shown by an analysis of KURODA and SANDELL, may also contain chlorine: in one sample of fluorite (the locality being given simply as "England") they reported 170 ppm Cl.

Among pure chlorine minerals, sodalite, $Na_3Al_6Si_6O_{24}Cl_2$, may occur in basic eruptive rocks, and according to this formula should contain 7·32 per cent Cl. But since the mineral forms solid solutions with haüyne and nosean, it usually contains less chlorine than this. Finally, one should also mention the scapolites, mix-crystals which, according to TRÖGER, contain 0·1–2 per cent Cl; the pure end members do not occur in nature. The scapolites play a very subordinate role in magmatic rocks. Bromine and iodine form no minerals of their own in magmatic rocks; and their occurrence can only be explained as attempted below in sections 2–4.

The mineral apatite which is widely distributed in all magmatic rocks, has long been recognized as a carrier of fluorine and chlorine. Analyses of apatites from magmatic rocks were made by KIND, and are quoted in Table 5, where they are supplemented by an older analysis of an apatite from a pegmatite near Bamle given by VON FELLENBERG and LUNDE (1927) as well as by two new analyses by BEHNE.

KIND alleged that the apatites in basic rocks were richer in chlorine than those of acid rocks. It should be noted that in his diagram (which is reproduced

Table 5. Halogen Contents of Apatites in ppm

Source	F	Cl	Br	I	Authority and remarks
Granite, Lausitz, Saxony	13,500	800			KIND
Monzonite, Ehrenberg, Thuringia	25,200	2,100			KIND
Sodalite-syenite, Schwaden, Czechoslovakia	19,800	1,500			KIND
Ijolite, Jiwaara, Finland	18,300	1,300			KIND
Olivine-nephelinite, Rossberg, Odenwald	17,200	9,600			KIND
Essexite, Rongstock, Czechoslovakia	25,600	3,300			KIND
Yellow apatite, Bamle, Ödegarden, Norway	(0–16,600)	(8,100–58,000)		0·78	F, Cl: from HINTZE I: v. FELLENBERG and LUNDE
Apatite, Jumilla, Spain		5,630	5·5		BEHNE
Apatite, Floitental, Tyrol		530	1·3		BEHNE

here as Fig. 1) he has made use of an apatite analysis by STELZNER (1889), containing 3·5 per cent F, instead of the apatite from the Lausitz granite, which he had analyzed himself, containing 1·35 per cent F. Our text Fig. 1 contains both analyses. It seems to me to be doubtful whether KIND's conclusion, which has been widely quoted in the literature, is really valid. In any case, one can draw no firm conclusions about chlor-apatite in magmatic rocks from these investigations. These seem to be restricted to pegmatitic-hydrothermal occurrences, as for example at Bamle, Ödegarden. Further investigations of apatites from magmatic rocks appear to be necessary.

Pure fluor-apatite, according to the formula $Ca_5(PO_4)_3F$, should contain 3·77 per cent F; pure chlor-apatite 6·80 per cent Cl. In fluor-apatite there

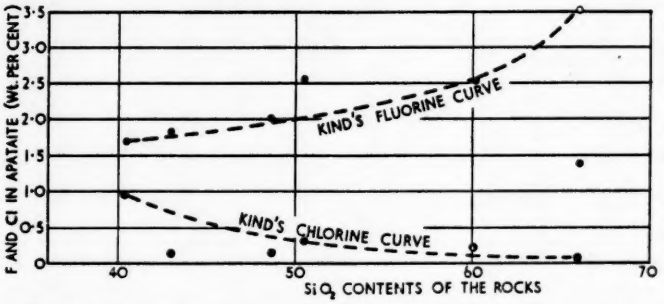

FIG. 1. Fluorine and chlorine contents of magmatic apatites, after KIND. F contents (Kind) — ●; F content of apatite quoted by KIND from Stelzner — ○; Cl contents (Kind) — ⊕.

is 11·2 P_2O_5 to 1 F, in chlor-apatite 6·0 P_2O_5 to 1 Cl. In addition most magmatic apatites contain some OH, so that the figures given above are to be regarded as maxima. If one uses these maxima to see how much of the fluorine and chlorine content of the rocks in Tables 3 and 4 might be present in apatite, one usually finds that there is more fluorine and chlorine than can possibly be present in this mineral. Only in such rocks as the oligoclase-andesine-basalt (mugearite) (Table 4) from New Zealand, the analysis of which is given by TURNER and VERHOOGEN, after BENSON, is it possible that all the fluorine and chlorine are present in apatite; this is also the case in kimberlite, in the basalt of the Hoher Hagen, near Göttingen, in the limburgite of New Zealand, and at least approximately so in Icelandic basalts investigated by BARTH. In the remaining rocks in Tables 3 and 4, the phosphorous content is not sufficient to explain the total content of halogen. There must, therefore, be other possibilities.

2. The halogens may replace other ions in crystal lattices. It has long been recognized that micas may contain fluorine, which can replace the OH^- ion. Fluor-phlogopite was synthesized some time ago (see for example KOHN and HATCH). Table 6 shows in what sort of amounts fluorine and chlorine may enter into the structures of natural micas. Biotite, phlogopite, and especially lepidolite may show much higher values than muscovite. SERAPHIM is of the opinion that this is to be attributed to the fact that the OH^- ion in these minerals is less strongly polarized than in muscovite, and can therefore be more easily

Table 6. Halogen Contents of Micas in ppm

	F	Cl	Br	I	Authority and remarks
Muscovite in: 168 samples Mean:	1,000–14,800 2,360				HEINRICH, 1953
Granite, Rautenkranz, Erzgebirge		20			BEHNE
6 Granites Mean:	170–7,700 1,690				SERAPHIM
Granite, Webb Quarry, Marlboro', N.H.	200				SERAPHIM
Pegmatite, Webb Quarry, Marlboro', N.H.	170				SERAPHIM
Pegmatite, Petaca, New Mexico Mean:	6,500–14,800 10,000				HEINRICH, 1953
Pegmatite, Minas Geraes, Brazil	2,900	350	3		KORITNIG, BEHNE
Pegmatite, Halvorsröd, Radde Östfold, Norway				0·69	v. FELLENBERG and LUNDE, 1927
Biotite in: Granite, Schierke, Harz	4,150				KORITNIG
Granite, Teufelsberg, Odenwald		530	4·3		BEHNE
Granite, Rautenkranz, Erzgebirge		650	5·9		BEHNE
6 Granites Mean:	950–35,000 14,500				SERAPHIM
Quartz-diorite, Capilano, Vancouver, B.C.	2,600				SERAPHIM
Gabbro-diorite, Salem, Mass.	970				SERAPHIM
Pegmatite, Webb Quarry, Marlboro', N.H.	9,500				SERAPHIM
Pegmatite, Grenville, Ontario	14,000				SERAPHIM
Pegmatite, Brooks, Mt. Seward Peninsula, Alaska (Siderophyllite)	50,000				SERAPHIM

Table 6. (contd.)—

	F	Cl	Br	I	Authority and remarks
Tonalite, Cairnsmore of Carsphairn complex	23,800				Nockolds and Mitchell, 1948
Granite, Cairnsmore of Carsphairn complex	16,900				
St. Lawrence Co., N.Y.		1,100			Kuroda and Sandell
Biotite from Quartz-monzonite, Rockville, Minn.		1,800			Kuroda and Sandell
Kragerö, Norway			5	0·5	v. Fellenberg and Lunde, 1927
Phlogopite in: Bamle, Ödegarden, Norway				0·63	v. Fellenberg and Lunde, 1927
"Phlogopite"		600			Kuroda and Sandell
Phlogopite, Mte. Somma	25,700				Pieruccini
Snake Creek, Utah	3,300				Heinrich
Perth, Ontario Centre:	27,000				Heinrich
Margin:	37,000				
Lepidolite in: Pidlite dike, Mora County, New Mexico	54,000				Jahns
26 Samples	19,000–68,000				Heinrich
Mean:	54,100				
Lepidolite, Black Hills, S.D.		310			Kuroda and Sandell
Protolithionite, Greisen Eibenstock	35,000				Koch and Teuscher

replaced by the less polarizable F^- ion. This finding is supported by observations of Butler (1953), who found the biotite and muscovite of an adamellite from Bosahan, Lizard area, Cornwall, to contain 19,600 ppm and 4000 ppm F respectively.

Table 6 shows further that micas may at the same time contain appreciable quantities of chlorine. While the ionic radius of the F^- ion is similar to that of the OH^- ion, that of Cl^- is appreciably greater: $OH^- = 1{\cdot}33$ kX, $F^- = 1{\cdot}33$ kX, $Cl^- = 1{\cdot}81$ kX. Goldschmidt's observation in his posthumous book: "But we never observe the presence of chlorine in such hydroxy-silicates as the micas, amphiboles, or humites into which fluorine enters very freely," stands therefore in need of correction in the light of the newer analyses. Judging from the single determination made on a muscovite from granite, it appears that the chlorine

content must be very low. The "muscovite" from the pegmatite of Minas Geraes, Brazil, of which a full analysis was made in the Göttingen Institute, contains 4·73 per cent Fe_2O_3, 1·11 per cent FeO, and 0·64 per cent MgO. Further determinations of chlorine in micas ought to be made.

In addition the hornblendes may contain fluorine and chlorine in place of the hydroxyl ion, as is shown in Table 7. The amounts are of the same order of magnitude as in the common micas, in the case of chlorine sometimes being higher than in these latter. This is apparently connected with the band structure of the hornblendes, which is better able to accommodate the appreciably larger

Table 7. Halogen Contents of Hornblendes in ppm

Rock and Locality	F	Cl	Br	I	Authority and remarks
Granite, (ferrohastingsite), North-west Adirondacks	9,600	6,000			BUDDINGTON, 1953
Younger granite, North-west Adirondacks	15,000	3,700			BUDDINGTON, 1953
Gabbro, Burlington, Pennsylvania	7,300	600			ROSENZWEIG and WATSON
Rapakivi granite, Finland	10,600	5,100			SAHAMA, 1947
Granite, Stearns Co., Minn.		1,800			KURODA and SANDELL
Sagenaga granite, Minn.	3,000				SERAPHIM
Rhode Island granite (Riebeckite)	10,000				SERAPHIM
Quincy granite, Mass.	29,000				SERAPHIM
Pulaskite, Fourche Mt., Arkansas	3,500				SERAPHIM
Quartz-monzonite, Lincoln Co., Nevada	2,100				SERAPHIM
Diorite, Snake Butte, Harlem, Montana	800				SERAPHIM
Syenite-porphyry, Madison, Montana	1,000				SERAPHIM
Nepheline-syenite, Magnet Cove, Arkansas	1,100				SERAPHIM
Analcite-labradorite-syenite, Big Bend, Texas	270				SERAPHIM
Granite, Teufelsberg, Odenwald		530	4·2		BEHNE
Amphibole-andesite, Stenzelberg, Siebengebirge		210	2·8		BEHNE
Kragerö, Norway			10	0·16	v. FELLENBERG and LUNDE, 1927

Cl^- ion. Further analyses of hornblendes with high fluorine content will be dealt with below in the section on metamorphism.

When biotite and hornblende are present in the same rock the fluorine content of the biotite is generally—but not always—higher than that of the hornblende, as is shown in Table 8.

Table 8. Fluorine Contents (in ppm) of Biotites and Hornblendes from the same Rocks

Rock	Biotite	Hornblende	Authority
Tonalite, Green Valley, Cal.	2,200	1,700	LARSEN and DRAISIN
Lakeview Tonalite, Cal.	13,700	1,800	LARSEN and DRAISIN
Bonsall Tonalite, Cal.	700	900	LARSEN and DRAISIN
Bonsall Granodiorite, Cal.	5,800	2,300	LARSEN and DRAISIN
Woodson Granodiorite, Cal.	3,200	2,100	LARSEN and DRAISIN
Rubideaux Granite, Cal.	2,100	12,000	LARSEN and DRAISIN
Quartz-free Alkali syenite, Katnosa, Nordmarka, Norway	5,000	10,000	BUTLER, 1954

There is a further mineral in which fluorine has been detected, but which, in spite of its wide distribution, especially in granodioritic plutonic rocks, seldom makes any significant contribution to their overall fluorine content, yet is none the less of interest because it provides an example of fluorine replacing oxygen. This is sphene (titanite), CaTi O[SiO_4]. JAFFE found fluorine contents between 1200 and 4700 ppm; SAHAMA (1946) between 1000 and 1400 ppm; SERAPHIM between 2700 and 10,000 ppm. According to SAHAMA (1946) the fluorine replaces the first oxygen in the formula, some of which can also be replaced by OH^-. The substitution of chlorine has not been demonstrated with certainty.

The mineral cancrinite $(Na_2,Ca)_4[CO_3|(H_2O)_{0-3}|(AlSiO_4)_6],)$ which is sometimes present in appreciable quantities in foyaitic and theralitic plutonic and hypabyssal rocks, may also contain limited quantities of chlorine. A recent analysis by PHOENIX and NUFFIELD gave 4500 ppm Cl in an occurrence at Blue Mountain, Ontario.

In the majority of cases, we may now make a reasonable attempt to explain the fluorine and chlorine contents of rocks in terms of the minerals we have been discussing. We may select the following examples from those given by KORITNIG:

Brocken granite, Schierke im Harz.—The rock has a fluorine content of 0·086 per cent. The biotite, the modal quantity of which corresponds to 7·0 per cent by weight, has a fluorine content of 0·415 per cent. Calculation gives:

	Per cent F
7·0 weight per cent biotite with 0·415 per cent F contributes to the rock	0·029
0·11 weight per cent fluorite (by difference) contributes	0·053
Apatite (1/12 P_2O_5) contributes	0·004
Yielding together the determined amount of F	0·086

The calculated fluorite content agrees very well with the evaluation of this mineral in grain counts of the heavy mineral fraction (approx. 0·1 per cent).

Opdalite, Ulsberg, Norway. Apart from apatite only biotite is present in this rock as a possible carrier of fluorine. Fluorite could not be detected in the heavy mineral fraction.

The rock has a fluorine content of 0·066 per cent. By grain counts and by measurements on the heavy mineral fraction, it contains 12 weight per cent of biotite. Calculation gives:

	Per cent F
1/12 P_2O_5 (corresponding to 0·6 weight per cent apatite) contributes . .	0·021
12 weight per cent biotite, with 0·38 per cent F (estimated by difference) contributes	0·045
Totalling together the determined quantity of	0·066

Tonalite, Adamello, South Tyrol. In this rock, as well as apatite, biotite and hornblende are the chief carriers of fluorine.

The rock contains 0·034 per cent fluorine, and according to measurements made on thin sections and from weighings and grain counts of the heavy mineral fraction, contains 32 weight per cent of dark green hornblende and 22 weight per cent of a brown-green biotite. Fluorite was not observed. Calculation gives:

	Per cent F
1/12 P_2O_5 (corresponding to 0·19 weight per cent apatite) contributes .	0·006
54 weight per cent hornblende and biotite contribute the difference, assuming an average content of 0·05 per cent F	0·028
Total	0·034

The syenite of Zitschewig near Dresden, contains as well as apatite, 21 weight per cent of hornblende as a major carrier of fluorine; no fluorite was detected in the heavy mineral fraction. The rock contains about 1 per cent of sphene (according to a microscopic analysis by O. BRAITSCH), which could also contribute about 0·01 per cent to the fluorine content. For this reason, the fluorine content of the hornblende, estimated by difference, may be somewhat too high. Calculation gives:

	Per cent F
1/12 P_2O_5 (corresponding to 0·5 weight per cent apatite) contributes . .	0·018
21 weight per cent green-black hornblende with a fluorine content, estimated by difference of 0·042 per cent contributes to the rock	0·088
Totalling the determined fluorine content of	0·106

In an average mixed sample of the Harzburg gabbro, also, apatite is not the only carrier of fluorine. Preparations of the crushed rock showed the presence of 8 weight per cent of brown biotite, which may also contribute. Other fluorine minerals, in particular fluorite, were not observed. Further, this mineral has not yet been detected in the well known gabbro quarries of the Radautal. Calculation gives:

	Per cent F
1/12 P_2O_5 (corresponding to 0·13 weight per cent apatite) contributes .	0·005
8 weight per cent brown biotite with a fluorine content, estimated by difference, of 0·44 per cent contributes	0·035
Totalling the determined fluorine content of	0·040

The fluorine content of the biotite, estimated by difference, agrees fairly closely with the fluorine content of a biotite from the Radautal, Harz, analysed by STRENG, who found 0·36 per cent F.

KURODA and SANDELL give five examples for chlorine content, of which two are reproduced below.

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Table 9. Chlorine Balance of Two Rocks (after KURODA and SANDELL)

Rock	Mineral	Percentage of rock	Cl in mineral	Absolute percentage Cl contributed to rock	Cl in rock by direct analyses
Hornblende granite, Stearns Co., Minn.	Hornblende (+ biotite)	7	0·18	0·013	
	Feldspar (mostly K)	80	0·014	0·011	
	Quartz	10	(0·00)	0·00	
				0·024	0·020
Quartz monzonite, Rockville, Minn.	Microcline	35	0·014	0·005	
	Plagioclase (An 28)	35	0·028	0·010	
	Biotite*	7	0·18	0·013	
	Quartz		0·002	0·001	
				0·029	0·032

* Includes 1 per cent hornblende, traces of zircon and apatite.

These examples are of particular interest in showing that in these acid rocks, apatite plays no appreciable part as a carrier of chlorine, as was also deduced from KIND's analyses. In KURODA and SANDELL's analyses, further, the chlorine content of feldspars and quartz is of interest. In this case we are dealing with yet another possibility for the occurrence of the halogens:

3. Inclusions in minerals. These may either be solid, for example inclusions of fluorite, mica or apatite; or fluid, which are very abundant in quartz and feldspar. In Table 10 are given several analyses of minerals in which there is some suspicion that the halogens are present in inclusions. BEHNE, as well as KURODA and SANDELL, has pointed out that in these instances we may be dealing with fluid inclusions. In any event we know very little about the composition of the fluids in the inclusions, or about their amounts. The most

Table 10

	F	Cl	Br	I	Authority and remarks
Feldspar, Granite, Rautenkranz, Erzgebirge		60	≦ 1		BEHNE
Microcline-perthite, Halvarsröd, Norway			5	0·37	v. FELLENBERG and LUNDE, 1927
3 potash feldspars		50–180			KURODA and SANDELL
Albite, Halvarsröd, Norway			2	0·15	v. FELLENBERG and LUNDE, 1927
Labradorite, Soggendal, Ekersund, Norway			20	0·44	v. FELLENBERG and LUNDE, 1927
Bytownite, Crystal Bay, Minn.		50			KURODA and SANDELL
Enstatite, N.C.		110			KURODA and SANDELL
Hypersthene, Nain, Labrador	[300]*	220	[8]	[0·94]	Cl: KURODA and SANDELL F: LOKKA Br, J: FELLENBERG and LUNDE, 1927
Diopside, Hull, Quebec		340			KURODA and SANDELL
Diallage, Sonoma Co., California		90			KURODA and SANDELL
Diallage, Gabbro, Radautal, Harz		≦ 20			BEHNE
"Augite"	100–1000				F: TRÖGER
Quartz, Granite, Rautenkranz, Erzgebirge		≦ 20	≦ 1		BEHNE
Smoky quartz, Halvarsröd, Norway			< 2	0·33	LUNDE and v. FELLENBERG, 1927
Quartz with liquid inclusions		30			KURODA and SANDELL

* Figures in brackets refer to material from a different locality.

important work is that of FABER (1941), who tried leaching rocks and minerals with water, and was always able to detect chlorine in the resulting solutions. We may suspect however that chlorine may be leached out into solution from the apatites as well as from the micas, so that FABER's values for the "locked" chlorine in rocks are perhaps somewhat too high. Thus BEHNE found that, in shaking up the biotite of the Rautenkranz granite with water for two hours,

60 ppm Cl went into solution; the original chlorine content of the biotite was 650 ppm. In the case of the feldspar from the same rock, all the chlorine (60 ppm) went into solution with this treatment, and was therefore presumably present in inclusions. Bromine behaves in a similar way. Therefore only the figures for quartz and feldspar taken from FABER's data are quoted below.

Table 11. Soluble Chlorine in Quartz and Feldspar (calculated in ppm) from Analyses by FABER

	Cl
Quartz, Arendal (Gloserhei), Norway	120
Feldspar, Arendal (Gloserhei), Norway	80
Quartz, Barhult, Sweden	150
Feldspar, Barhult, Sweden	60

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Admittedly these analyses refer to minerals from pegmatites, and thus belonging to the post-magmatic phase, but we can certainly reckon with amounts of the same order of magnitude in magmatic rock minerals as well. This is confirmed by leaching experiments carried out by KURODA and SANDELL. In 7 magmatic rocks which they investigated, they found amounts lying between 0 and 60 ppm of soluble Cl—between 0 and 28·6 per cent of the total chlorine content. The investigations of GROGAN and SHRODE show that the chlorine content of fluorite, discussed above, page 188, may depend upon fluid inclusions: it is true that they only found qualitatively appreciable quantities of chlorine. Unfortunately there are no determinations available for the other halogens.

We must always take into account solid inclusions as well as fluid. Thus SERAPHIM considers the fluorine content of 1000 ppm in a diopside from de Kalb, N.Y. to be due to inclusions of biotite. Inclusions of mica in feldspars are very well known.

It is difficult to decide how far the observed quantities of bromine and iodine are to be explained in terms of replacement of the smaller OH^-, F^-, or Cl^- ions by the larger ions of these elements, with radii of 1·96 and 2·20 kX respectively, rather than by inclusions. Most likely would seem to be a replacement of chlorine, with its relatively large radius of 1·81 kX, by bromine and iodine. As far as the present rather meagre data show, the content of these elements in quartz and feldspar is of the same order of magnitude as in apatite and in the sodalite of Brevik, Norway, in which VON FELLENBERG and LUNDE found 2 ppm Br and 0·9 ppm I. In hypersthene (Soggendal, Norway) the same authors found 8 ppm Br and 0·94 ppm I. There is thus apparently no enrichment of bromine and iodine in chloro- or hydroxyl-minerals (see also Tables 5, 6 and 7). The contents of all these minerals correspond roughly with the contents of the rock, giving weight to the possibility that bromine and iodine remain behind in the residual liquids and enter into fluid inclusions with the mother liquor. This is certainly also the case with a small proportion of the chlorine. The newer analyses show very clearly, however, that the main part of the chlorine is built into crystal structures in place of F^- or OH^-.

4. A further possibility for the occurrence of the halogens is in rocks which contain glass, in which these elements may remain dissolved. Table 12 gives

Table 12. Rock Glasses

	F	Cl	Br	I	Authority and remarks
Obsidian, Iceland				0·32	v. FELLENBERG and LUNDE, 1926
Obsidian, Hruni, Iceland		80	2·1		BEHNE
8 Obsidians (v. ENGELHARDT)		240	1·4		BEHNE
Obsidian, Teneriffe		1280			BEHNE
6 Obsidians, Little Glass Mount, California	450	627			SHEPHERD,
3 Obsidians, Coso Mts. California	1000	800			SHEPHERD. Cl only determined in 1 sample
Obsidian, Naivasha, Africa (Rift Valley). Coll. N. L. BOWEN	6850				SHEPHERD
Phonolithic trachyte pitchstone, Lake Baringo, E. Africa	1500	1100		P_2O_5 1600	BOWEN
Retinite (Obsidian), L'Esterel, France	500	300		200	WYART

the halogen contents of several glassy rocks. The wide range of variation among different examples is very striking. Apparently the amount of halogen incorporated depends very much on the conditions of formation. The six analyses of glasses from Little Glass Mount, very similar in their chemical compositions, also show very restricted variations in their contents of fluorine and chlorine. BEHNE's value for bromine in the eight obsidians seems rather high; unfortunately only one determination of iodine has been made.

CLARKE and WASHINGTON (1924) calculated a value of 300 ppm F as an overall average for magmatic rocks; this figure was calculated from the phosphorus content of the rocks because of the uncertainty of fluorine determinations at that time. In 1940, SHEPHERD assessed this average fluorine content at 400 ppm; WASSERSTEIN (1946) maintains that the value of 300 must be doubled, and BARTH (1947) agrees with him with a value of 800 ppm F. KORITNIG, on the basis of his own analyses, takes a value of 700 ppm F. SERAPHIM arrives at a very similar value to that of KORITNIG, namely, 670 ppm F. In the case of chlorine, CLARKE and WASHINGTON (1924) took a value of 480 ppm. SELIVANOV (1940) gives 314 ppm Cl and 1·62 ppm Br as averages. From SELIVANOV's data, BEHNE calculated 392 ppm Cl and 3·6 ppm Br, taking into account his own estimates of the relative abundance of the various rocks. On the basis of his own analyses, BEHNE finds as an average only 150 ppm Cl and 3·1 ppm Br. KURODA

and SANDELL give 200 ppm Cl as an average. For iodine there are no new estimates; GOLDSCHMIDT's figure in 1933 (quoted again in GOLDSCHMIDT, 1954) was 0·3 ppm I.

III. POST-MAGMATIC OCCURRENCES (PNEUMATO-HYDATOGENIC AND EXHALATIVE)

Reference should be made to the more recent text books (e.g. BARTH, 1952; CORRENS, 1949; TURNER and VERHOOGEN, 1951) for discussions of the processes, based upon general laws of physical chemistry, which control the formation of watery residual solutions from a magma and their ultimate behaviour. In these sources will also be found information about the behaviour of fluorine and chlorine. These elements form compounds which are readily volatile, and, in the case of chlorine, also readily soluble in water. As BUERGER (1948) was able to demonstrate, they are also of significance in explaining the behaviour of a silicate melt, since the replacement of oxygen by OH^-, F^- or Cl^- at the corners of the $[SiO_4]$ tetrahedra hinder their polymerization and hence the formation of glass; this in turn reduces the viscosity and aids the formation of crystals.

If we now consider the pegmatites, we find as well as fluorspar, topaz, $Al_2[F_2|SiO_4]$, as an independent fluorine mineral. This has a theoretical content of 21 per cent F, but usually contains only between 20·5 and 15·5 per cent, because in this mineral F^- may be replaced by OH^-. In addition tourmaline may occur, whose formula in the ideal case may be written (according to HAMBURGER and BUERGER) $NaMg_3Al_6[(OH)_4|(BO_3)_3|Si_2O_{18}]$. In this case it is not the substitution of cations which is of chief interest, but rather that of OH^- by F^-, which may take place up to an extent of 10,000 ppm. The chlorine content of 60 ppm in a tourmaline reported by KURODA and SANDELL may perhaps be due to inclusions.

The micas of pegmatites may also have a high content of halogens (see Table 6). Phlogopites and lepidolites from pegmatites are also included in Table 6 and are especially rich in fluorine. The lithia-micas in the table, with their high values for fluorine, also come from pegmatites.

Alterations brought about in a granite itself, and in country rock, by such vapours and gases—for example greisen formation—will be dealt with in Section VIII, on metamorphism.

The pegmatites grade by way of tourmaline-quartz-gold veins into hydrothermal mineral deposits, in which fluorite may be present as an accessory constituent and more seldom as a major constituent. It is often a matter of some doubt to try to delimit those occurrences which have obtained their material from neighbouring rocks by a process of lateral secretion. As far back as 1917 KÖNIGSBERGER discussed the question of lateral secretion for the fluorine in the Alpine mineral vein paragenesis, and considered it likely that these had a mixed origin. In 1940, NIGGLI came down on the side of lateral secretion, making the observation that 1 cubic metre of Aar granite contains 0·67 kg F, corresponding to 18 kg apatite, or 1·3 kg fluorite: a fraction even of these quantities would be sufficient to explain the fluorite content of the Alpine mineral veins, ignoring also the possibility that the mica might contain fluorine as well. Studies of the fluid inclusions in ore minerals (see, for example,

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NEWHOUSE) show that chlorine bearing solutions have contributed in the formation of hydrothermal ores. For general geochemistry, these occurrences are not of any great significance.

On the other hand, volcanic exhalations are extremely important, and their contribution to the halogen economy of the earth in the total of geological time must not be undervalued. Thus ZIES has estimated the annual production of HCl and HF in the Valley of Ten Thousand Smokes in the Katmai district of Alaska, an area of only 77 sq. km, at $1{\cdot}25 \times 10^6$ tons and $0{\cdot}2 \times 10^6$ tons respectively. Unfortunately, very few other determinations of fluorine in volcanic gases have been made. According to ALLEN (1922) the ratio by weight of Cl to F in the gases of the Devil's Kitchen, Hawaii, is 6·5:1, almost the same as at Katmai. At the surface of the crust the various halogens will behave differently: fluorine, which occurs as HF in such volcanic gases, will very soon be combined in the difficultly soluble CaF_2; while chlorine on the other hand is able to remain in aqueous solution as the ion. I do not know of any analyses for bromine and iodine in volcanic gases. In two alkaline hot springs in Iceland, BARTH (1950) found 1·45 and 0·55 ppm F (mg/L water), these figures being thus within the concentration range for fresh water. In the sea water geyser of Reykjanes, BARTH found 77 ppm Br, the ratio Br:Cl being 1:330; in sea water it is about 1:293, nearly the same. In weakly alkaline hot springs in French Somaliland, East Africa, AUBERT DE LA RÜE found the following Cl and Br contents: at the shore of Lac Abbé, Cl 1048 ppm, Br 2·7 ppm; and in the springs of Aguena near Hanleh, Cl 910 ppm, Br 2·4 ppm. The ratio of Br:Cl is 1:388 and 1:379 respectively, and thus still of the same order of magnitude as in sea water. VON FELLENBERG (1924) determined the iodine content of certain Swiss mineral waters, finding values between 0·01 and 6·3 ppm I; this must certainly not be regarded as directly due to the emission of gases from a magma. However, analyses by Stoklasa show that iodine does occur in volcanic exhalations. In the lava of Vesuvius he found 1 ppm I, and in crystals of NH_4Cl found in drusy cavities in the lava, 1·28 ppm. He also found 1 ppm I in encrustations of sulphur, gypsum and alum at the Solfataras in the neighbourhood of Naples. FOSHAG and HENDERSON (quoted from BARTH, 1952) found besides 63·78 per cent Cl, 0·88 per cent F in sublimates of the volcano Paricutin in Mexico. Chlorine and fluorine compounds occurring as sublimates and encrustations are known from many volcanoes (see, for example, CLARKE).

Two pieces of work in recent years have considered the contribution which these gases make to the chlorine content of sea water, and they both come to the conclusion that an appreciable fraction is contributed in this way. The first of these is by RUBEY (1951): the other is the investigation of KURODA and SANDELL, which has already been referred to frequently. The following calculation and table is taken from that source. The total content of the oceans today carries $2{\cdot}8 \times 10^{22}$ grams of chlorine. If this has been accumulated in the course of 3×10^9 years, then roughly 10^{13} grams of chlorine must have been contributed each year.

Table 13 shows that even the sources mentioned therein may contribute about 13·3 per cent of the total chlorine taken into the oceans. And even if some of the hot springs contain no juvenile chlorine, but only originally oceanic chlorine, then it must be remembered that there are numerous other volcanic exhalations to take into account. On the other hand, the amount of 10^{13} grams

of Cl contributed per year is certainly too low, because a part of the chlorine of the ocean remains in sediments.

Table 13. Annual Chlorine Yield of some Magmatic Sources (in grams) (from KURODA *and* SANDELL)

	Cl produced per year	Percentage of total yearly requirement
Kilauea	3×10^{10}	0·3
Valley of Ten Thousand Smokes (1919)	$1{\cdot}3 \times 10^{12}$	13
Norris Geyser Basin, Yellowstone Park	1×10^{9}	0·01
Steamboat Springs, Nevada	$3{\cdot}5 \times 10^{9}$	0·035
Arima, Hyogo Perfecture, Japan*	$1{\cdot}5 \times 10^{9}$	0·015

* The water flow of this spring is conservatively estimated at 100 tons per day; Cl = 40 g per litre.

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IV. PRODUCTS OF WEATHERING AND SOILS

The behaviour of fluorine in weathering is discussed in two important new papers by BUTLER, from which the data in Table 14 have been taken. In the case

Table 14. Behaviour of Fluorine in Weathering (after BUTLER)

	Fluorine in ppm
Bosahan adamellite, Lizard area, Cornwall	1,000
Contained muscovite	4,000
Contained biotite	19,600
Soil below 12 in.	
Contained weathered biotite	500
Contained silt	500
Contained saturated clay	500
Quartz-free alkali, syenite Katnosa, Nordmarka, Norway	300
Contained hornblende	10,000
Contained biotite (8·9% K_2O)	5,000
Soil:	
Contained weathered biotite (4·8% K_2O)	5,000
Contained Ca-saturated clay	2,000

of the Cornish adamellite the greater part of the fluorine has vanished. In addition, most of it has been leached away from the weathered biotite. In the Norwegian profile, on the other hand, fluorine has very largely been retained; in the biotite all of it. This may perhaps be explained by the F^- ion replacing the OH^- ion in the octahedral layers, where it is linked with Fe^{2+} ions. In the warmer climate of Cornwall, conditions of weathering would be such that the leaching out of Fe^{2+} would take place more readily than in the cold climate of Norway, while there the K^+ ion would also be removed. Apart from the question of the mica, the fluorine content naturally also depends upon the phosphoric

acid content. There is an extensive literature about the reciprocal relationship between fluorine and phosphoric acid in soils, but this cannot be gone into here.

ROBINSON and EDGINGTON have determined fluorine in a large number of soils. In the majority (17) of profiles, they found a decrease in fluorine from below upwards; in a single profile they found the reverse relationship; in 8 profiles the fluorine content was very nearly constant; in 4 profiles it reached a maximum in an intermediate position. These investigations, also, show that the behaviour of fluorine may be different under different conditions of weathering. MICHAEL and BLUME (1952) investigated the fluorine contents of Muschelkalk and Bunter sandstone soils in Thuringia. In 7 Muschelkalk soils they found between 630 and 3680 ppm F, in 11 Bunter sandstone soils between 90 and 880 ppm F.

Table 15, after VINOGRADOV* (1954), gives a review of the data on the fluorine content of soils.

KORITNIG and BEHNE have determined the content of fluorine, chlorine and bromine (Table 16) in a weathering profile of the St. Andreasberg granite which

Table 15. Fluorine Contents of Soils from Different Countries, in ppm (from Vinogradov)

Country	Number of analyses	Fluorine content min-max	Average Fluorine content	Author
U.S.S.R.	46	30–320	200	VINOGRADOV and DANILOVA, 1947
U.S.A.	16	100–1,500	250	STEINKOENIG, 1919
	16	80–340	150	MCINTIRE, 1942
	137	10–7,070	290	ROBINSON and EDGINGTON, 1946
New Zealand	23	68–540	200	GEMMEL, 1946

Table 16. Halogen, P_2O_5 and C-contents (in ppm) in a Weathering Profile at St. Andreasberg

Depth below surface	F	P_2O_5	F not combined with P_2O_5	Cl	Br	C
1/2–1 m	50	310	24	20	8·3†	1200
1–2 m	20	280	0	140	6·0	
2–3 m	30	270	10	670	5·8	
3–5 m	40	390	10	600	3·4	
Fresh Brocken granite, Schierke	860	500	820	270	1·2	30

* In German spelt Winogradow; see List of References.
† 2·6 ppm leachable.

was investigated mineralogically by PILLER (1951). In this neighbourhood the granite is so deeply weathered that no fresh rock was encountered in the profile. A fresh sample of the Brocken granite from Schierke is incorporated in the Table for purposes of comparison, but naturally the possibility cannot be ruled out that the St. Andreasberg granite had originally a lower content of halogens than the Schierke granite. Since, however, the granites always have a higher content of fluorine than is found at the deepest point, 3–5 m, of a profile (see Table 3), it may be assumed that at this place the fluorine has been removed from the rock at a very early stage—and that essentially all the fluorine has been removed from the micas. The trend of the phosphate contents show that at least half, and sometimes appreciably more than half, of the fluorine remaining is present in apatite; this is in agreement with the microscopic observation that apatite is still present in the weathered soil. Chlorine goes appreciably more slowly, first of all from the higher horizons, more or less parallel with the bleaching process of the biotite. In the highest horizon of all it was no longer detectable. Bromine, on the contrary, is enriched in the weathering products. Apparently we are dealing here with some sort of combination with organic substances. The enrichment of bromine by means of organic matter was confirmed by KREJCI-GRAF and LEIPERT in 1936. It is not yet clear whether this enrichment results from the formation of chemical compounds or by a process of adsorption (VINOGRADOV, 1954). In the highest horizon of the profile, which contained 8·3 ppm Br, Behne was able to leach out 2·6 ppm with water: 31 per cent of the total bromine content. A large proportion at least of the bromine is thus bound in such a state that it cannot be leached away. According to VINOGRADOV (1954) bromine enrichment is generally found in the humus horizons, while the ratio Cl:Br falls. Apart from humus, the bromine content is also dependent upon the type of soil formation, which is very clearly demonstrated by some examples (Table 17) which have been taken from VINOGRADOV's book (1954).

These examples give at the same time a measure of the chlorine and iodine contents of these Russian soils. I do not know of any further recent researches into the chlorine content of products of weathering.

A proportion of the halogens which are found in soils does not originate directly from weathering, but is contributed by rain water; this question is dealt with in more detail below. It is very difficult to make any estimate of how great this contribution may be. At any event, the available researches show that the essential part of the halogens in soils comes from weathering.

There are very many older works dealing with the behaviour of iodine, which were summarized in a book by SCHARRER (1928). In general an enrichment of iodine is to be observed in soils, especially in the uppermost layer (Table 17). On the basis of adsorption experiments VON FELLENBERG came to the conclusion that the iodine had its origin in rain water and found its way into the soil either directly or by way of plant remains. In 1930 a paper by CAUER was published, reporting the results of studies of the iodine content in a series of rocks and soils. In the A-horizons (uppermost layer) he found iodine contents of 3·9, 2·7, and 2·4 ppm I, falling within the range of values given by VINOGRADOV (Table 17). In a basalt from Breungeshain in the Vogelsberg he found 0·54 ppm I, in the decomposed rock 1·34 ppm, and in the resultant earth, from which rootlets were removed by sieving, 2·69 ppm I.

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Table 17. Chlorine Content of Soil Profiles (in ppm of Dried Soil) (*from* VINOGRADOV, 1954)

Soil type	Soil horizon	Cl	Br	I	Cl:Br	Br:I	C
Podsol upon varved clay	A_2	40	2·48	3·6	17	0·7	0·13
	B	70	0·44	1·1	160	4	0·10
Grey forest soil	A_0	35	5·69	6·7	6	0·85	3·73
	A_1	30	0·66	4·2	46	0·16	1·0
	B	30	0·6	2	50	0·30	0·39
	C	20	0·33	0·67	60	0·50	0·0
Sandy black earth	A	45	·7	5·5	6·3	1·2	3·69
	B	35	3·5	4·3	10	0·8	1·49
Desert grey earth	A	35	0·98	1·3	35·7	0·7	0·32
	B	370	0·43	3·8	860	0·11	0·03
Red earth beneath Rhododendron forest	A	100	25	11·8	4	2·4	10·8
	B	55	4·8	7·2	12	0·7	0·0
Mountain tundra soil	A_0		17·8	12·7		1·4	17·8
	B		2·9	1·8		1·5	5·48
	C		2·2*	3		0·7	2·50

* VINOGRADOV's original has "$2{\cdot}2 \times 10^{-3}$ per cent"; the Br:I ratio, however, gives $2{\cdot}2 \times 10^{-4}$ per cent.

I should like to add to this discussion of soils a few remarks about bauxites, which are admittedly not "soils" in the pedological sense, but are at least in part products of weathering. KORITNIG found 90 ppm F and 490 ppm P_2O_5 in a white bauxite from Eplèny in Hungary; in the same material BEHNE found 1200 ppm Cl (of which only 66 ppm could be leached out by water) and 2·3 ppm Br. On account of this strikingly high content of chlorine, he later investigated 8 further bauxites from different countries, which yielded chlorine contents of between 80 and 780 ppm, of which between 15 and 87 per cent was leachable. The unleachable chlorine amounted to between 10 and 280 ppm. As far as both the magnitude of its chlorine content and its leachibility are concerned, therefore, the bauxite originally investigated remains so far unique.

V. HYDROSPHERE AND ATMOSPHERE

The halogens find their way from the soil into ground water and into the rivers. The fluorine content of ground waters and of rivers has been mainly investigated from a medical point of view, since too high a content of fluorine in drinking water may give rise to harmful effects in man and in animals; too low a fluorine content, on the other hand, may have a harmful influence on the growth of teeth (caries). The review by BROMEHEAD of the state of affairs in Great Britain concludes that fluorine contents above 1·2 ppm may be harmful. The "ideal" fluorine content appears to be between 0·3 and 0·5 ppm. MÖSE and EXNER (1952) state that in 110 samples of Styrian drinking water over 75 per cent had a fluorine content below 0·1 ppm, and that only one sample reached the 0·8 ppm which they regard as necessary for effective prophylaxis against caries. D. TOMIĆ (1951) found 1–11·6 ppm Cl and 0·035 and 0·12 ppm F in drinking, river, and lake waters in Montenegro. One spring at Ulcinj yielded 1600 ppm Cl and 0·95 ppm F. SUGAWARA gives values of 32·1–55·4 ppm F (mg/L) for the Osama spring of Sakunishi Hot Springs; in the Yukawa river 12 ppm F, and after its confluence with the Shibukuro-gawa river 5 ppm F. In Nigeria, WILSON found 0·1–0·4 ppm F in 9 samples of waters from a basalt-capped granite plateau, and 0·1–1·2 ppm in 6 samples of waters from the crystalline basement complex.

STROCK was able to demonstrate that the Saratoga Springs, N.Y., were conditioned by ascending water which had taken up halogens and other elements at various points on its way. Table 18, after STROCK, shows the variability in halogen content of the Saratoga springs; this variability is not only in the total concentration of dissolved substances, but in the ratios of the halogens one to another.

Table 18. Halogen Content (mg/l) and Ratios in Saratoga Waters (calc. from Analyses in Spa Information Booklet) (after STROCK*)*

Spring	Cl	Br	I	Cl/Br	Cl/I	Br/I
Geyser	1,701·0	22·2	1·25	76·7	1,360	17·8
Coesa	3,222·0	11·1	1·56	290·0	2,060	7·1
Hathorn No. 2	5,691·0	110·0	3·76	51·2	1,510	29·6
Hathorn No. 3	5,377·0	22·2	0·31	242·0	17,350	71·5
Hathorn No. 1	3,563·0	15·6	0·78	228·0	4,575	20·0
Lincoln	2,085·0	13·9	trace	150·0	—	—
Hayes	3,867·0	20·8	1·0	186·0	3,867	20·8
Karista	2,049·0	15·3	1·37	134·0	1,500	11·2
Old Red	573·0	8·7	0·39	66·0	1,470	22·3
Coesa (S.D.—7/8/38)	2,969·0	9·4	1·04	315·0	2,860	9·3
Coesa (LWS—7/12/40)	3,160·0	27·2	—	116·0	—	—
(Sea water)	19,300·0	66·0	0·05	292·0	386,000	1,320·0

HEIDE and KAEDING have recently determined the contents of all four halogens in a river water, giving the following values for yearly averages in the Saale at Göschwitz, a little above Jena (Table 19).

Since many factories lie on the upper Saale, the possibility of contamination

Table 19. Halogen Contents of Saal River Water, after HEIDE *and* KAEDING. *Yearly Average at Göschwitz in ppm (mg per litre)*

Fluorine	Chlorine	Bromine	Iodine
0·26	18·5	0·0106	0·0022

cannot be ruled out. BEHNE found 2·5 ppm Cl and 0·006 ppm Br in the river water of the Grosse Bode, 2·5 km above Braunlage in the Harz mountains; this water certainly contains no contamination and comes from a moor which lies upon Brocken granite. The average chlorine content for river waters given by CLARKE depends upon the value assumed for the salt content of the river waters of the earth, and lies between 5·68 ppm Cl with a salt content of 100 ppm, and 8·3 ppm Cl with a salt content of 146 ppm. CONWAY is in agreement with the latter value. GOLDSCHMIDT (1934) puts the average value for iodine in river water at 0·0007–0·003 ppm. From the rivers the halogens find their way into the sea, in which according to WATTENBERG (1943) there is 1·4 ppm F, 65 ppm Br and 0·050 ppm I. If the total salt content of the ocean is 3·433 per cent, then 19,000 ppm Cl are present. If for river water we take CONWAY's value for chlorine, BEHNE's value for bromine, HEIDE's for fluorine, and for iodine an average based upon GOLDSCHMIDT's mean value of 0·0018 ppm, then we obtain the figures given in the following table for the relative enrichment of the halogens.

Table 20. Halogen Contents of River and Sea Water, in ppm

	Fluorine	Chlorine	Bromine	Iodine
River water	0·26	8·3	0·006	0·0018
Sea water	1·4	19,000	65	0·05
Concentration factor in sea water	5·4	2,290	10,800	27·8

It is evident that they are all concentrated, fluorine the least, and bromine—5 times more strongly than chlorine—the most.

The behaviour of sea water in sediments is also of importance from the point of view of the circulating water in rocks. EMERY and RITTENBERG have investigated marine ground water in recent sediments off the coast of southern California. They found that the ratio $Cl:SO_4$ was higher in the water in the pore spaces of the sediment as compared with sea water, because SO_4 is reduced in the sediment. For example, the ratio $Cl:SO_4$, which is 7·15 in sea water, rose to 33·3 at a depth of 70 in. in the sediments of the sea floor. In the deep-sea sediments off the north Brazilian coast, on the other hand, LOCHER found the ratio to change in favour of SO_4. At depths between 236 and 585 cm in the sediments the ratio $Cl:SO_4$ varied between 3·72 and 4·51. Apparently no reduction had occurred in this case; perhaps LOCHER's result may be explained

in terms of the uptake of chlorine by clay minerals, as is indicated by experiments made by BEHNE (see below). Under no circumstances can we depend on an unaltered marine salt content in fossil sediments.

Completely different concentration relationships may be obtained in inland waters than in the ocean; depending upon the catchment area certain ions may be more abundant and others rarer. An interesting example is provided by the Dead Sea, which is fed by the River Jordan.

Table 21. Contents of Anions in the Dead Sea, River Jordan and the Ocean, in percentage of the Total Salt Content (after CLARKE; *Analyses since* 1880)

	R. Jordan	Dead Sea			Ocean
Cl	41·47	64·49	63·40	65·86	55·292
Br	—	1·45	1·69	1·13	0·188
I	—	—	—	$2{\cdot}47 \cdot 10^{-5}$	—
SO_4	7·22	0·45	0·42	0·39	7,692
CO_3	13·11	—	trace	0·02	0·207
Cl:Br		44·5	37·5	58·3	294

We can see that in this case a much more striking enrichment in bromine has taken place than in ocean water. CLARKE also gives data for the bromine content of other inland seas, which range from 0·04 to 0·22 per cent of the total salt content. In all these examples the ratio Cl:Br is always greater than in ocean water.

An appreciable proportion of the halogens of river waters does not originate directly from weathering, but is brought to the surface of the land along with rain water. The halogen content of rain water originates from the sea; perhaps by tiny droplets of foam being caught up by the wind, or perhaps, as suggested by CAUER (1938) for the case of iodine, the halogen ions are oxidized by means of ozone and liberated into the atmosphere in the form of gas. E. ERIKSSON (1952) has provided a new summary of the data for the composition of atmospheric precipitates, including in particular data for chlorine and iodine. BEHNE has found 0·7 ppm Cl and 0·008 ppm Br in rain water at Göttingen—the ratio Cl:Br here is 87, while in sea water it is 292. According to CONWAY $0{\cdot}69 \times 10^{14}$ grams Cl are deposited annually upon the continents; this is appreciably more than the annual amount contributed to the oceans, according to the calculation on page 200. We cannot here embark upon a discussion of this "cyclic salt"; the reader is referred to the works by CONWAY, RUBEY, and KURODA and SANDELL.

Industrial gases may also liberate fluorine into the atmosphere—from coal, and for example, as pointed out by BROMEHEAD, in firing a clay with 550 ppm F in the manufacture of tiles. In cases like this, the surrounding grassland may become so heavily poisoned with fluorine, that harm may be done to animals.

The iodine contents of the atmosphere and rain water have been much discussed. Reviews were given by ERIKSSON (1952) and V. M. GOLDSCHMIDT (1954). The ocean is undeniably a principal source; apart from this, iodine is liberated into the atmosphere by industrial gases and in the process of ashing seaweed in the commercial production of the element. GOLDSCHMIDT points out that in salt deposits the ratio Cl:I is greater than in sea water, so that iodine may be lost by vaporization from sea water. It will be shown below, in a discussion of salt deposits, that this assumption is a rather dubious one. The iodine content of the atmosphere varies independently of the height between 0·1 and 1·4 mg/m^3, while the Cl content, on the other hand, appears to decrease with height. Further, the ratio Cl:I in rain water is very much lower than in sea water. Both these observations seem to indicate that gaseous iodine is present, and besides, one must assume the presence of iodine in sea water droplets. From the presence of iodine in rain water, too, we must suppose that it can be liberated into the atmosphere as a gas. We may conclude from these observations that the behaviour of iodine is different from, and appreciably more complicated than, that of chlorine. GOLDSCHMIDT stressed the need for further investigations, especially above the oceans and in the tropics.

VI. BIOSPHERE, COAL AND PETROLEUM

Plants and (either directly or indirectly) animals take up halogens from the soil and waters. In the case of chlorine this has long been recognized. As far back as 1828 SPRENGEL (quoted by ROBINSON and EDGINGTON) suggested that fluorine also might be taken up through the agency of plants, because of its occurrence in bones and teeth.

In 28 dried samples of plants and plant organs, ROBINSON and EDGINGTON, using improved methods, found Cl contents varying from traces below the limit of detection (fruit of tomato) and 42·3 ppm (young shoots of poke), the average value being 6·75 ppm Cl. There are some plants which contain even greater contents of fluorine, as for example, tea, which may contain up to 400 ppm F.

In 120 samples of coals from the British Commonwealth, CROSSLEY found 0–175 ppm F, the majority containing less than 80 ppm. Etching was noted in glass-making furnaces where coals containing 85–135 ppm F were used. The strata lying immediately above and below the coals contained up to 480 ppm F. Leaching experiments, as well as comparisons with the phosphorus content, indicate that fluorine in coal is present in apatite.

It has long been known that chlorine is taken up by plants, and in consequence is also contained in coals. At my request, BEHNE (unpublished) has determined the chlorine content of certain coals: in bituminous coal from upper Bavaria he found 200 ppm Cl; in a hard coal from Upper Silesia 10 ppm Cl, and in lignite from Westerwald 10 ppm Cl. These determinations are not very reliable because, on digestion of the sample with NaOH, tarry products are formed, which cannot be removed and which colour the solution brown, so that the subsequent titration is rendered difficult, if not impossible.

Bromine is also taken up by plants. SCHARRER (1944) quotes values from DAMIENS for *Raphanus sativus* of 8 ppm, for *Boletus scraber* of 36 ppm, and for *Curcuma citrullus* of 262 ppm Br. KREJCI-GRAF and LEIPERT found 5·12 ppm Br

in an upper Carboniferous semi-bituminous coal from Unna, and in another upper Carboniferous boghead coal from Marl (seam 15) 4·75 ppm Br.

Numerous older determinations of the iodine content of plants are available. CAUER (1930), for example, found 6·2 and 6·4 ppm I in rootlets, and 13·45 ppm I in grass in the soil profile described earlier (page 17). In peat, J. MCCLENDON (quoted by GOLDSCHMIDT, 1954) found 12–40 ppm I, in coals 1·6–11 ppm. WETZEL (in STUTZER) quotes values from KÖHLER of 3·2–4·1 ppm I for brown coal from Lausitz; and 2·1–3·2 ppm I in hard coal from South Africa. From WACHE he quotes values of 1·32 ppm I in hard coal from Silesia, and 0·9–1·26 ppm I in hard coal from central Germany. In this connection it seems to me to be worth mentioning that an attempt was made in Germany during the Second World War to recover iodine from light blast-furnace ashes. MIDDEL reports that the iodine had its source in the coke used; the blast-furnace dust carried between 10 and 2000 ppm I.

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All three halogens are further found in animal organic matter. For example, human teeth contain 300 ppm F. The fluorine content of land animals is appreciably smaller than that of sea creatures (KLEMENT, 1938), (Table 22).

Table 22. Average Fluorine Contents of Bones and Teeth of Land and Marine Animals, in ppm (after KLEMENT)

	Land	Marine
Mammals	500	5,500
Birds	1,100	3,200
Fishes	300	4,400

The bones and teeth of marine animals are thus about ten times richer in fluorine than those of land animals. KLEMENT has further established that bones and teeth (dentine and enamel) have the same fluorine contents. Supplementary uptake of fluorine by bones and teeth buried in soil has been established, and the magnitude of the fluorine content can be used as an indication of their age. In these cases, phosphate of the skeletal parts reacts with the fluorine present in the soil solutions. GOLDSCHMIDT (1954) expresses doubt as to the possibility of age determination by this method.

Very few data for the fluorine content of invertebrates are available. As for the other halogens in marine organisms, these have been taken, unless stated to the contrary, from the English translation (1953) of VINOGRADOV's memoir. The highest fluorine contents are shown by the brachiopods. The shell of a recent *Lingula anatina* from Ceylon contained 52·1 per cent organic matter and 47·9 per cent ash, which contained 1·52 per cent (= 15,200 ppm) F and 42·99 per cent P_2O_5. In the ash of fossil *Obolus* shells, different authors found 2·78 per cent and 3·31 per cent F, as well as 36·54 per cent and 36·57 per cent P_2O_5. Obviously, this high F content is related to that of P_2O_5; apatite could be detected in the shells by means of X-rays. However, in phosphate-bearing shell ash of other organisms, especially of crustaceans, no fluorine has as yet been reported; 30 and 120 ppm F have been reported in shells of *Ostrea edulis*, and likewise 30 and 120 ppm F in shells of *Mytilus edulis*. In *Ostrea* shells also,

CHATIN and MUNTZ found 150–200 ppm F. The land snails *Limnea*, *Planorbis* and *Helix* also contain 30 ppm F. In 1865 MOHR reported traces of fluorine in Foraminifera; since then no new investigations have been made. About 10 ppm F were found in the calcareous alga *Lithothamnium* from the Gulf of Kola. In all these cases, with the exception of the brachiopods, no enrichment of fluorine has taken place. Chlorine is contained in the body fluids and tissues of animals and plants; KALLE gives 10^{-1}–10^{-2} per cent Cl as an average concentration in living matter.

As shown above, bromine and iodine are concentrated in sea water, and they may be further enriched in marine organisms. Iodine was discovered in the ash of seaweed by COURTOIS in 1812, and is produced commercially from this source. The Phaeophyceae are especially rich in iodine. For example 1080–17,000 ppm I were found in dried material of *Laminaria digitata*, and 8400–55,000 ppm I in the plant ash. The same species contains 1200 ppm Br in the dried material, while other Laminarias contain 400–780 ppm Br. Rhodophyceae contain up to 4510 ppm I in dried material, *Fucus vesiculosus* 10–1000 ppm. The iodine content of Chloropyhceae is generally less, but may reach as much as 1460 ppm in dried material. Figures of 40 and 50 ppm I were recorded for dried planktonic Cyanophyceae from the Sea of Azov, where they contribute organic material to the recent sediments. A value of 80 ppm I has been given for a fresh-water species. Marine diatoms, which are very important sediment builders, generally contain about 30 ppm I in the dried material, rising to 620 ppm I in the Caspian Sea; fresh water diatoms contain up to 10 ppm in dried material. In sponges, Low found 500–12,100 ppm I in dried material, and 0–26,000 ppm Br. In the coral family of the *Gorgonidae* values of 200–7790 ppm I and 2300–2610 ppm Br have been determined in dried material. In the marine snail *Murex brandaris*, bromine is secreted in the form of the organic complex 6—6′—dibromoindigotin, which upon oxidation by the atmosphere forms a purple dyestuff which was much used in ancient times (Tyrian purple). *Vermes* contain traces up to 6500 ppm I and 20–3190 ppm Br. In the reef-building coral *Aeropora varia* from the Mediterranean, VON FELLENBERG (1924) found 0·4 ppm I in inorganic combination, and 2 ppm I in organic combination; the total was 2·47 ppm. Of 44 ppm I in *Corallium rubrum* about half was in inorganic and half in organic combination. An oyster from the Mediterranean contained 4·08 ppm I, of which 0·1 ppm was in the inorganic state.

Bromine and iodine are also found in the vertebrates, the latter being concentrated in the thyroid gland.

KREJCI-GRAF and LEIPERT found 1·6 ppm Br in the crude petroleum of Zistersdorf near Vienna; 1·46 ppm in Iraq petroleum; 1·6–3·3 ppm Br in German petroleum. In asphalt from Bentheim, northern Germany, they found 3·42 ppm Br; in oil distilled from the bituminous marl of Seefeld, Tyrol, 1·98 ppm; and 3·3 ppm Br in Kukersite oil shale from Estonia. Bromine and iodine are enriched in the saline waters which accompany petroleum. These waters contain the bromine and iodine of the organisms which went into the formation of the oil. KREJCI-GRAF (1930) for example, quotes figures of 330–390 ppm I and 6500 ppm Br in such residual waters from Filipesti in Rumania, and from Bordeni 350 ppm I and 410 ppm Br. ROEBER found 11·4 and 1·5 ppm I in petroleum saline waters from Volkenroda, corresponding to 24·7 and

3·1 ppm I respectively in the evaporated residues. In salt water from Nienhagen he found 4·0 and 9·1 ppm I, corresponding to 32·8 and 37·1 ppm I respectively in the evaporated residues.

VII. SEDIMENTS

Included here under the title "Sediments" are all transported and stratified products of mechanical and chemical weathering of rocks, and of their transporting media (BARTH, CORRENS, ESKOLA). Thus coals are dealt with under the biosphere, bauxite under weathering and soil formation. Among the sediments then we have:

1. The residues of weathering, which may be chemically unaltered, like grains of quartz, or which may be partly decomposed, like micas, which may occur in all stages of disintegration.
2. New products from weathering, e.g. clay minerals formed in the soil, and further colloidal materials—as for example, iron hydroxide.

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These substances are transported mechanically and form the major ingredients of the clastic sediments, which may be divided up according to their grain size: here we shall distinguish only the psammites with an average grain size $> 0{\cdot}02$ mm, and the pelites with a grain size $< 0{\cdot}02$ mm.

The material which goes into solution during the processes of rock weathering may be re-precipitated by biological agency or by purely chemical means, e.g. by reactions, or through the evaporation of the solutions. In some cases, e.g. silicic acid, no sharp distinction is possible between solution and colloid. Further, chemical and biogenic constituents may occur in clastic rocks; and conversely clastic materials in chemical and biogenic sediments. Moreover, since in many instances the relative proportions of biogenic and purely chemical material are in doubt, we shall group these sediments below into chemical-biogenic, and shall separate them only from the evaporites of undoubtedly chemical origin.

In addition, newly-formed substances in sediments must be taken into account; these again may have either a biological origin, e.g. sulphides, or may arise by chemical reactions, e.g. clay minerals. It is frequently impossible to distinguish detrital material from material which has been altered or freshly formed within the sediment.

(*a*) *Clastic Rocks*

A glance at Table 23 shows that in the psammites the fluorine cannot only be present in apatite, but must also be present in the micas. SERAPHIM found 70 ppm F in an impure quartzite from Lake Athabasea, which is less than the average given by KORITNIG; on the other hand he found appreciably more in the greywackes of the same locality, namely 480, 320, and 200 ppm F. These variations are very simply explained in terms of the remarks made earlier concerning the weathering of micas, which according to circumstances may either give up or retain their fluorine. The behaviour of apatite on weathering is also variable. As well as this, differing conditions of deposition will give rise to varying quantities of fluorine-bearing minerals in the sedimentary rocks. KORITNIG found 4540 ppm F in the muscovite of a sandstone from the middle Bunter; the measured muscovite content of the rock (1 per cent) thus yields 45 ppm F to the rock; similarly apatite (1/12 P_2O_5) yields 20 ppm. This still leaves a deficiency of 15 ppm in the measured fluorine content of the rock,

Table 23. Halogen and Phosphorus Contents of Psammites, after KORITNIG (F and P_2O_5) *and* BEHNE (Cl and Br)

Rock	F	Cl		Br	P_2O_5
		Total	Leachable		
Average of 23 German Bunter sandstones (v. ENGELHARDT)	450				450
Average of 11 German Carboniferous sandstones (v. ENGELHARDT)	320				760
Average of 11 German Cretaceous sandstones (v. ENGELHARDT)	280				200
Average of 10 German quartzites (v. ENGELHARDT)	200				320
Koblenz quartzite, Krebsberg bei Urbar, Rhineland		20	5		
Middle Bunter sandstone, Reinhausen b. Göttingen	80	20		≤1	220
Calcareous sand, Meteor Station 219; 220 m depth	190				
Average of 17 German greywackes (v. ENGELHARDT)	40	100		12	940
Kulm* greywacke, Lauterberg, Harz	80				300
Tanner greywacke, Scharzfeld, Harz, coarse		70		3·9	
Tanner greywacke, Scharzfeld, Harz, fine		20		2·8	
Loess, Hedemünden b. Göttingen	360	20	8	≤1	1,360

* The original paper describes this erroneously as "Tanner" greywacke.

which KORITNIG computes as present in 0·003 weight per cent fluorite. Fluorite has been found abundantly in clastic sediments, see for example BOSWELL. Topaz also is observed from time to time. KORITNIG however remarks that the small difference of 15 ppm could be accounted for by experimental error either in the determination of the mica content of the rock or in the determination of fluorine.

The Loess contains a large amount of phosphoric acid, but even this is insufficient to explain its fluorine content.

Chlorine is low throughout the sedimentary rocks. KURODA and SANDELL found 20 ppm Cl in the St. Peter standstone of Minnesota. Bromine contents are of the same order of magnitude as for the magmatic rocks, which is also true for iodine. VON FELLENBERG found 0·8 ppm I in a Schilfsandstein (Keuper),

0·32 ppm I in a sandstone of the lower fresh water Molasse, and 0·7 ppm I in a sandstone from the marine Molasse of Switzerland. WILKE-DÖRFURT found 0·02 ppm I in a Stubensandstein from the Keuper, while CAUER (1930) gives values of 0·5–0·8 ppm I in four samples of the Taunus quartzite.

Table 24. Halogen Contents of Pelites (in ppm) after KORITNIG *and* BEHNE

Rock	F	Cl		Br		P_2O_5	Cl: Br
		Total	Leachable	Total	Leachable		
Diluvial clay, Papendorf bei Rostock, Mecklenburg	630	220	≤10	1·7		970	129
Septarian clay, Middle Oligocene, Mallis, Mecklenburg	990	450	450	58	58	870	7·9
Lias clay, Dobbertin, Mecklenburg	760	210	165	5·2		1,270	40
Laminated marl, Upper Muschelkalk, Diemarden b. Göttingen	1,780	210	70	5·5	1·7	1,370	38
Clay bed in Middle Bunter sandstone, Fredelsloh, Lower Saxony	1,180	170	33	3		820	57
Middle Oligocene glauconitic clay, Lemke brickworks, Ülsen, Lower Saxony	550	60	30	≤1		470	
Wissenbach shale, Middle Devonian, Rammelsberg, Goslar, Harz	960	50	33	4·2		1,230	12
Green Keuper clay, Friedland, S. of Göttingen	690	370	54	4·4		780	84
Sea water, for comparison							294

The analyses of KORITNIG for F and P_2O_5, and of BEHNE for Cl and Br in the fine-grained pelites (consisting predominantly of clay minerals) are grouped together in Table 24, since the figures refer partly at any rate to rocks which have been investigated mineralogically. For instance, the Diluvial clay of Papendorf (SCHLÜNZ, 1933; BARTH, CORRENS and ESKOLA) contains 4·4 per cent hornblende, 2 per cent biotite, 30·5 per cent muscovite, and 7 per cent montmorillonite. KORITNIG takes a fluorine content of 0·15 per cent for the first three minerals, and 0·125 per cent for the montmorillonite and, together with the apatite (calculated from the P_2O_5 content) is able to arrive at the total fluorine content of the rock. The septarian clay of Mallis (SCHLÜNZ, 1933;

BARTH, CORRENS and ESKOLA) has 25·4 per cent muscovite or illite, which must have a fluorine content of 3700 ppm if, together with 30 per cent halloysite with an assumed fluorine content of 1700 ppm and the apatite, the total fluorine content of the clay is to be explained. Similarly, in the liassic clay of Dobbertin (SCHLÜNZ, 1935; BARTH, CORRENS and ESKOLA), the 53·6 per cent mica must contain 1100 ppm F and the 17 per cent kaolinite 600 ppm. A blue clay from the Cambrian of Estonia contains 1080 ppm F, and 390 ppm P_2O_5. It contains (PRALOW; BARTH, CORRENS and ESKOLA) 2·8 per cent biotite, 37·7 per cent "mica," and 18·5 per cent montmorillonite, which must carry about 2100 ppm F. Unfortunately there are very few fluorine determinations available for the clay minerals (Table 25); none have been made for illites.

Table 25. Halogen Contents of Clay Minerals

	F	Cl		Br		Cl:Br	Authority
		Total	Leachable	Total	Leachable		
Kaolinite, Dobritz Saxony	260						KORITNIG
Kaolinite, St. Austell, Cornwall	2,400						API 49 8% Sericite
Kaolinite, Schönhaid, Fichtelgebirge, Bavaria		290	80				BEHNE
Halloysite, Lawrence County	180	350	210	12	5	29	KORITNIG BEHNE
Montmorillonite, Heufeld b. Rosenheim, Bavaria		30					BEHNE
Bentonite, East Kentucky	4,100						SERAPHIM
Hydrous mica, Platteville, Wis.	5,800						ROBINSON and EDGINGTON
Sericite, Guanajuato, Mex.	1,800						ROBINSON and EDGINGTON
Sericite, Staley, N.C.	300						ROBINSON and EDGINGTON

The hydrous mica and perhaps also the sericite given in the table are similar to illites. The fluorine contents of bentonites, which originate from volcanic

material, are very high: ROBINSON and EDGINGTON give values of 4500 and 7500 ppm F. It must also be pointed out that values for hydrothermal kaolinites do not appear directly applicable to sedimentary clay minerals.

The following may also be quoted from KORITNIG's data: in 36 palaeozoic clay-slates (NOLL) 760 ppm F, 1170 ppm P_2O_5; in 14 Japanese palaeozoic clay-slates (NOLL) 500 ppm F, 420 ppm P_2O_5; in 10 Japanese Mesozoic clay slates (NOLL) 570 ppm F, 1050 ppm P_2O_5; in gypsiferous clay slate of Röt Eddigehausen near Göttingen, 50 ppm F, 250 ppm P_2O_5. SERAPHIM's determinations in slates gave similar results, lying between 1200 and 400, with an average of 9 determinations giving 750 ppm F. In 3 slates SHEPHERD found 240–330 ppm F.

SHEPHERD was also the first to investigate recent deep-sea sediments, and in an average of 34 analyses found 430 ppm F. In the Carnegie collection of samples of Globigerina ooze, the values range between 100 and 530 ppm F; in Red Clay between 330 and 1140 ppm. In two samples from the deep sea floor, SERAPHIM found no correlation with depth within the sediments of 3·55 m, 6·60 m, and 8·7 m. Of these samples the average of 8 analyses of the shallowest yielded 1520 ppm F; the average of 17 analyses from the middle sample yielded 540 ppm and the average of 20 analyses from the deepest 1100 ppm F. This is rather more fluorine than SHEPHERD found. No suggestion can be put forward as to the reason for these differences without further data. The figures of SHEPHERD referred to were from Pacific Ocean sediments; however, the samples from the Atlantic Ocean and from Alaska which he analysed also gave fairly low results. Unfortunately, neither author gave any information about the contents of $CaCO_3$ and P_2O_5, which influence the F content. Furthermore, the fluorine content may well be dependent to some extent upon the rate of sedimentation, so that at the very least data about the depth of the water would have been desirable. In abyssal Red Clay in the central Atlantic Ocean, at Meteor Station* 283 (20° N latitude) and at a depth of 5729 m, KORITNIG found a lime content of 4 per cent with 670 ppm F and 1040 ppm P_2O_5. In a blue mud near the coast of the Gulf of Guinea, from a depth of 4668 m at Meteor Station 229, he found a lime content of 2·1 per cent with 730 ppm F and 1800 ppm P_2O_5. Globigerina ooze from a depth of 2271 m south of the Gulf of Guinea at Meteor Station 240 had a lime content of 64·3 per cent with 550 ppm F and 780 ppm P_2O_5 (lime contents and depth measurements are after CORRENS, 1937). This last sample really belongs to the class of calcareous sediments.

As shown by the example of the septarian clay from Mallis, the whole of the chlorine content of clays can often be leached out with water. On the other hand, in the Diluvial clay of Papendorf this element remains behind in the minerals, which is also the case, at least as far as the bulk of the chlorine is concerned, with the Keuper clay from Friedland, which contains a swellable chlorite (Corrensite) as a major constituent. It is often assumed that soluble chlorine is a residue from the sea water in which the clay was originally deposited. That this is not necessarily true is indicated, apart from the investigations already described, by the example of an undoubtedly fresh-water glass retort clay from Grossalmerode to the south of Göttingen, examined by BEHNE, who found 110 ppm Cl, of which 48 ppm were leachable with water; while the marine septarian clays of Oberkaufungen which outcrop nearby contain only 15 and

* Stations of the research ship "*Meteor*" during the German Atlantic Expedition.

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20 ppm Cl. All the chlorine in the clay containing 15 ppm is leachable; while this is true of only about half in the other.

The following observation by BEHNE is of interest in connection with the question of chlorine uptake by clay minerals. He took a sample of the very much decomposed granite from Schönhaid, which is almost completely altered to kaolinite, shook the material with dilute HCl for varying times, washed it on a filter until free from Cl and then determined the residual (unleachable)·chlorine content of the kaolinite. The rock contained 1400 ppm P_2O_5, with which a portion of the Cl is combined. After shaking for 25 hours with 0·01N HCl, only 160 ppm Cl remained of the 210 ppm originally present, because the apatite had been dissolved. After 264 hours shaking, however, the Cl content had risen to 275 ppm. Some uptake of chlorine by the kaolinite had thus clearly taken place. A similar increase in chlorine content was observed in a montmorillonite from Heufeld: on shaking for 200 hours with 0·01N HCl, the unleachable portion of Cl had risen from 20 to 85 ppm. Certainly then, part of the chlorine is present structurally in minerals, mostly combined in the micas, but this is generally the smaller proportion. In connection with soluble chlorine, one must bear in mind that the solutions present in the rock circulate, and that their compositions change by processes of diffusion.

KURODA and SANDELL reported values of the same order of magnitude as BEHNE: in shale 140 ppm Cl; residual clay 70; slate 70 and 230 ppm Cl.

In the case of bromine, KREJCI-GRAF and LEIPERT have already shown that this element occurs in unusually large quantities in clays which are rich in organic matter. As KREJCI-GRAF explicitly emphasizes, however, there is no correlation between the locale of deposition—marine, brackish or fresh-water—and the bromine content. The bromine is contributed to the sediment by organisms, the chief of which are algae. In pure mineral clays, these authors found 1·51–4·1 ppm Br, similar values to those given in Table 24. In 11 sapropelites they found 0–20 ppm Br, with an average of 5·62 ppm; in 8 gyttja samples, 1·68–132 ppm Br, with an average of 38·66 ppm. KREJCI-GRAF explains this result by suggesting that the decomposition of organic matter has gone further in the sapropelites than in the gyttja deposits. The fact that bromine in the ordinary sediments (Table 24) is always enriched relative to sea water, may have some connection with its uptake by organic substances.

Iodine is also enriched in clays through the agency of organic matter. This is particularly well shown by a profile in the oil-shales (Lias γ) of Mössingen, in which WILKE-DÖRFURT has examined both the oil and the iodine content (Fig. 2).

In the Hunsrück slate, a highly metamorphosed rock, CAUER (1930) found values between 0·2 and 2·2 ppm I; in the Taunus slate he found between 0·3 and 0·8 ppm I. He attributes the high values for iodine to enrichment from the soil. In Flysch shale, VON FELLENBERG found 0·2 ppm I, and in Neocomian shale 0·78 ppm I. A high iodine content can thus originate either during the process of sedimentation, by the agency of organisms, or else secondarily at the surface, where the element may be derived from soil. Apart from such cases it appears that the iodine content of argillaceous rocks is not appreciably greater than that of magmatic rocks.

Finally, mention will be made of a rock whose origin has been very much discussed. According to WAGENMANN the bituminous Kupferschiefer of the

lower Zechstein at Mansfeld contains an average of 1500 ppm Cl; while KREJCI-GRAF and LEIPERT report 8·7 ppm Br. At another locality, Albungen, KORITNIG found 650 ppm F. I. NODDACK gives without further comment 200 ppm F, 6000 ppm Cl (!), 40 ppm Br and 0·04 ppm I.

(b) Chemical-biogenic Rocks

Mention has already been made (page 215 above) of the fluorine content of Globigerina ooze. In this material KORITNIG found 550 ppm F, of which 100 was estimated to be present in the mica and 70 in apatite, the rest was taken to be present in fluorite. In the *Ceratites* limestone (Table 26) too, which according

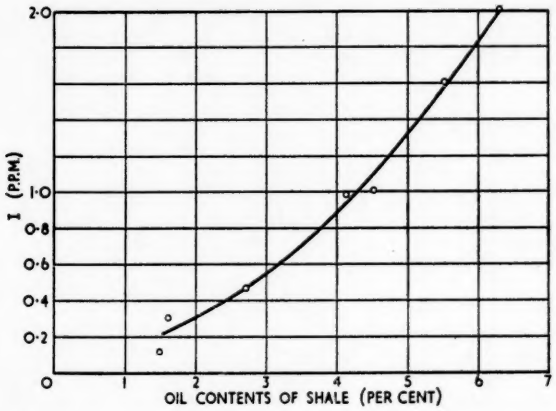

FIG. 2. Relationship between contents of oil and of iodine in Lias γ shales from Mössingen (after WILKE-DÖRFURT).

to FÜCHTBAUER contains about 1·5 per cent illite, an appreciable proportion of the fluorine must be assumed to be present as fluorite: KORITNIG estimates 370 ppm F, corresponding to 0·076 per cent fluorite. LUEDECKE has detected fluorite microscopically in such limestones. Similar considerations apply also to other limestones. Only in those cases where the presence of sufficient P_2O_5 can be demonstrated, as in the calcareous tuff of Lenglern, and in the Cenomanian pläner and in oolitic limestone, is it unnecessary to assume the presence of fluorite. Unfortunately, no investigations have been carried out on the solubility of fluorite in sea water, and even the data for its solubility in pure water deviate very widely. In German and American text books, e.g. D'ANS-LAX, the solubility of precipitated CaF_2 at 18°C is given as 0·0163 g/L and that of natural fluorite at 18°C 0·0158 g/L; SAHAMA (1945) however, proposes, after CARTER, an appreciably higher solubility of 0·04 g/L at 25°C. The value given by D'ANS-LAX for precipitated CaF_2 corresponds to 8·4 ppm F in pure water, while sea water contains only 1·4 ppm F. Nothing further can usefully be said about this question until there are further data for the solubility of fluorite in sea water. Unfortunately, there are no data either for the fluorine content of planktonic marine animals, especially for the foraminifera. In any event it is certain that limestones at least are relatively poor in fluorine. A few examples follow: average of 16 German Cretaceous limestones (VON ENGELHARDT)

Table 26. Halogen contents of Carbonate Rocks (in ppm) after KORITNIG *and* BEHNE

Rock	F	Cl		Br		P_2O_5
		Total	Leachable	Total	Leachable	
Recent calcareous tufa, Lenglern bei Göttingen	100	20		10·2	5·5	150
Chalk, Rügen	280	2,000	2,000	3·9		880
Cenomanian pläner, Kaierde, Hils, Lower Saxony	20	120	67	2·3		1,140
Oolitic limestone, Weissjura, Freden a.d. Leine, Lower Saxony	60	180	78	6		760
Ceratites limestone, Upper Muschelkalk, Diemarden b. Göttingen	510	240	110	4·9	1·6	1,260
Oolitic zone, Lower Muschelkalk, near Göttingen	190	50	20	6·8		350
Natural solution residue from Lower Muschelkalk, Göttingen	800	501	55	8·3		860
Zechstein dolomite, Scharzfeld, Harz	110	610	86	7·5	2·8	70
Zechstein dolomite, reef limestone, Römerstein b. Bad Sachsa, Harz. (Fluorite-bearing)	250	880	220	15	3·4	300

270 ppm F and 2360 ppm P_2O_5; average of 45 German Jurassic limestones (VON ENGELHARDT) 550 ppm F and 1970 ppm P_2O_5; average of 32 German Devonian limestones (VON ENGELHARDT) 210 ppm F and 450 ppm P_2O_5; Solenhofen limestone (Upper Jurassic) 120 ppm F and 200 ppm P_2O_5. In the Windsor limestones of Cape Breton, Nova Scotia, SERAPHIM found a maximum value of 1500 ppm F in the Ribben limestone, with sandy layers containing fluorite; in Magnesian limestone, south west Mabou, 700 ppm; in 6 other examples an average of 90 ppm. SHEPHERD found 370 ppm F in an argillaceous limestone, and in 2 fossiliferous limestones from Maryland 210 and 230 ppm F. In Ordovician limestones BARTH and BRUUN found 200 and 300 ppm F. It seems to me doubtful whether these limited amounts of fluorine are to be explained by the presence of fluorite, in so far as they are not combined in phosphate. So long as we have no data for the fluorine content of planktonic organisms, especially for foraminifera and coccoliths, the possibility remains that some of the fluorine has been taken into combination by organisms in their calcareous shells. The crinoidal limestone of Reckershausen, south of Göttingen, which is completely made up of crinoid stem columnals, contains only 20 ppm F with a P_2O_5 content of 380 ppm. This is an indication that these crinoids incorporated

no fluorine into their skeletons. In cases of exceptionally high fluorine contents, and where fluorite is visible either microscopically or with naked eye, one must bear in mind the possibility of migration of fluorine within the sediment, e.g. upon the solution of phosphate. Thus, the reef limestone in Table 26, in spite of a low fluorine content, carries crystals of fluorite.

The chlorine content of the calcareous sediments is partly leachable in water. In the sample of the Rügen chalk, quoted in Table 26, the whole of the chlorine could be washed out; while in another sample only 220 ppm Cl were present altogether. About half of the chlorine in the hard compact beds of the *Ceratites* limestone can be removed by leaching. The naturally-occurring insoluble residue of the Muschelkalk, consisting of mica and dolomite, gives an indication of the manner in which the chlorine is combined. On warming this residual material with 2N nitric or acetic acid, a total of 360 ppm Cl can be taken into solution. This was clearly contained in the dolomite, and the insoluble Cl content of the mica would then work out at the very possible figure of 300 ppm. The 55 ppm Cl which could be extracted by washing with water could come partly from the mica and partly from inclusions in the dolomite; perhaps part of it may be ascribed to the Cl content of rainwater. In any event, this example shows that, on crystallization, carbonates may include a certain amount of chlorine-bearing mother liquor. The high chlorine content of the dolomites and the fact that so little can be removed by washing with water is striking. On warming the Zechstein reef dolomite with 2N nitric or 2N acetic acid, the total chlorine content goes into solution. The insoluble residue in this case is less than 2 per cent, so that its chlorine content is not significant. Perhaps this also gives an indication of the nature of the solutions which bring about dolomitization. LAMAR and SHRODE also found water-leachable chlorine in limestones, and concluded that it was due to fluid inclusions, some of which they could actually observe in the rocks.

The bromine of these sediments does not show a parallel behaviour with that of chlorine. In this case the controlling factor must be the organisms whose remains become buried in calcareous oozes.

This also seems to be the case for iodine. In various Swiss limestones VON FELLENBERG found amounts varying between 0·25 and 0·75 ppm I; in the Triassic Röti dolomite 1 ppm I; in the Maltis limestone of the Kinzigpasshöhe 1·76 ppm; and in the Effingerschichten, likewise from the Malm (Upper Jurassic), 5·4 ppm I. A "petrefact" (no further details given) from these strata contained 9·2 ppm I. WILKE-DÖRFURT found up to 6·6 ppm I in the Malm of Württemberg.

Of the two siliceous rocks from the same section (Table 27), the one richer in mica has also the higher content of fluorine. The flint from the chalk contains very little fluorine, while the terrestrial diatomite contains none. It thus seems that the fluorine of the rock is contained in apatite and in micas and clay minerals. The low values for fluorine do not support the idea that volcanic exhalations are concerned in the formation of these cherts.

The chlorine contents are very low throughout; perhaps inclusions of mother liquor have only been partly released on pulverizing the material. According to BRAMLETTE, the chlorine contents of the siliceous Miocene deposits of the Monterey formation of California are very much greater. In 10 samples of diatomaceous rocks he found 13,400 ppm Cl, and in 10 samples of cherty shales 1600 ppm Cl. A "fairly soft cherty shale" contains 8100 ppm Cl, a

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Table 27. Halogen Contents of Siliceous Rocks, after KORITNIG *and* BEHNE

Rock	F	Cl		Br		P_2O_5
		Total	Leach-able	Total	Leach-able	
Chert† (grey-black), Kulm, Wallau, W. of Marburg	500	120	90	1		500
Chert† (yellowish), Kulm, Wallau, W. of Marburg	210	90	90	1		920
Chert†, Gelstertal	830	210	49	1		685
Flint, Upper Chalk, Rügen	40	330	18	1		520
Diatomite, Beuren, Vogelsberg	0	140	70	14	12	1,000

† "Kieselschiefer."

"very hard cherty shale" 2700 ppm Cl. VON FELLENBERG (1924) found 0·63 ppm I in flint from Rügen.

In the iron ores of the Lias-γ of Echte, examined petrographically by H. HARDER, KORITNIG found 160 ppm F together with 2010 ppm P_2O_5, and it seems as though the fluorine were combined with phosphate. In each of two samples BEHNE determined 170 ppm Cl, of which 90 ppm were leachable. The high phosphate content (which according to the figures given by HARDER amounted to 16,200 ppm in one and 12,700 ppm P_2O_5 in the other sample) may also be responsible for the chlorine, at least for that part which cannot be leached out.

The Br content of 3·5 and 4·5 ppm is perhaps due to organisms in this fossiliferous sediment. The same is also true of iodine. In the iron ores of the Dogger of Wasseralfingen (Württemberg) WILKE-DÖRFURT found 1·7–1·95 ppm I.

The significance of phosphate in combining with the halogens has been emphasized repeatedly. We would thus expect to find high contents of halogens in phosphate deposits. This has long been recognized for fluorine and there are very many analyses, for example those quoted by STUTZER, reporting quantities of 30,000 ppm and more. DIETZ, EMERY and SHEPARD found the quantities shown in Table 28 in recent phosphorites from the coast of southern California. According to the formula $Ca_5(PO_4)_3F$, the ratio $F:P_2O_5$ in pure fluorapatite should be only 0·0893. The Table 28 shows that more fluorine was found than corresponds to this formula, the authors explaining this by a substitution of O by F. A simple alternative could be, however, that a portion of the PO_4 is replaced by SO_4 or by CO_3.

A number of analyses have reported quantities of 1100 to 1600 ppm Cl. I have been unable to find data for bromine. WILKE-DÖRFURT investigated the iodine content of 16 phosphates, and in some of them found the element to be present in very large quantities. A Podolian phosphate contained 0·8 ppm I;

phosphates from Tunis, Algeria, and Tennessee gave 2·88, 2·87, and 2·6 ppm I respectively; 3 samples from Florida 3·75, 27·9, and 54·52 ppm I; a phosphate from Staffel an der Lahn gave 93·5 and a phosphorite from Limburg gave 280 ppm I. This last is the highest value found by WILKE-DÖRFURT.

Table 28. Fluorine and Phosphate Contents of recent Phosphorites, in percentage (from DIETZ, EMERY and SHEPARD)

	Station					
	69	106	127	158	162	183
P_2O_5	29·56	29·19	28·96	29·09	22·43	29·66
F	3·31	3·12	3·07	3·15	2·47	3·36
F/P_2O_5	0·1120	0·1069	0·1060	0·1082	0·1099	0·1132

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(*c*) *Evaporites*

Salt deposits of marine origin contain very large quantities of chlorine. KORITNIG has made some investigations on the occurrence of fluorine. In anhydrite of the Zechstein salt series he found 130, 800, 810, and 890 ppm F; the rocks contained very small quantities or no P_2O_5. Gypsum contained 130 and 870 ppm F. The anhydrite with 890 ppm F was a leached out residue from halite in older rock-salt. This rock-salt inclusive of residue contained 57 ppm F, while the halite separated from the residue contained only 7 ppm. Polyhalite contained 20 ppm, and potash salt 300 ppm F. KORITNIG is of the opinion that the fluorine in the potash salt is also present in anhydrite with which it is inevitably intimately admixed. The question arises as to the form in which the fluorine is present in anhydrite. At two localities, at the Gebroulaz glacier in Savoy and at Bleicherode am Harz, bituminous dolomite containing anhydrite carries sellaite, MgF_2. Since MgF_2 is appreciably more soluble than CaF_2, we may be fairly certain that in general it is fluorite which originally occurs in the anydrite, and that sellaite is a product of secondary alteration. Fluorite has not been detected microscopically, which is scarcely to be wondered at, since at most only about 1·8 mg would be present in 1 g of the anhydrite. It seems reasonable to assume that during the evaporation of sea water the fluorine —in so far as it had not already been precipitated along with the carbonates— would be precipitated with the $CaSO_4$, on account of the limited solubility of CaF_2. In present-day sea water, the ratio of SO_4:F is $2{\cdot}65:1{\cdot}4 \times 10^{-3}$; or $1{\cdot}9 \times 10^3$; 1 kg of anhydrite contains 700 g of SO_4, so that using this ratio, we would expect a fluorine content of about 370×10^{-3} g/kg (= 370 ppm F) of anhydrite, assuming that all the fluorine has been precipitated. Now, not all the sulphate is precipitated in anhydrite, yet the fluorine content of the latter is almost double that which we have calculated.

An average of 3 samples of anhydrite from Bad Sachsa, Harz, gave 190 ppm Cl (unpublished analyses made in the Mineralogical-Petrographic Institute, Göttingen).

I can find no data for the bromine content of anhydrites. On the other hand, H. E. BOEKE (1908) has discussed the bromine content of potash salts, which provide part of the European bromine requirement, in some detail. He showed that bromine could enter the crystal lattices of all chlorides in the place of chlorine, but in widely differing amounts. The substitution is least in the cases of NaCl and sylvine, KCl. Bischofite, $MgCl_2 . 6H_2O$ and carnallite, $KCl . MgCl_2 . 6H_2O$ form unbroken series of mix-crystals with their bromine analogues. Carnallite in salt deposits contains 2000–40000 ppm Br. D'ANS and KÜHN have studied the bromine content of NaCl, and have found quantities up to about 300 ppm. They have made use of such bromine contents to follow processes of recrystallization in salt deposits.

ROEBER (1938) published a detailed investigation on iodine in salt deposits, which supplements the older work. In anhydrites ROEBER found 0·0155–0·1365 ppm I. VON FELLENBERG had found 0·3 ppm I in the anhydrite of Bex. ROEBER found even smaller quantities in rock salt, samples of which in different grades of purity carried 0–0·051 ppm I; in sylvine he found up to 0·036 ppm, in hartsalz up to 0·0965 ppm, and in carnallite up to 0·029 ppm I. In red carnallite from Stassfurt, L. W. WINKLER found no iodine; in colourless carnallite he found 1·5 ppm, in grey 4·5 and in yellow 5 ppm I. He attributed the absence of iodine in the Fe^{3+}-bearing red carnallite to the decomposition of iodides by oxidative processes. Subsequent workers have not confirmed these high iodine contents given by WINKLER.

BOEKE (1908) concluded that no mix-crystal formation took place between iodide and chloride. From our more modern point of view, this is quite understandable, in view of the great difference in ionic radius: $Cl^- = 1·81$ kX, $I^- = 2·2$ kX. According to BOEKE the iodine of sea water should remain behind in the residual solutions left over after crystallization. In a "primitive liquor" from Lübtheen in Mecklenburg, which had a very high content of Mg and Cl, KOELICHEN found a ratio Br:I of 3960:2·7(= 1467); in sea water this same ratio is rather lower, 1300, which is to be explained by some bromine entering the salt structure. In any case it is difficult to say whether this is really a residual liquor, or a circulating solution, which may have acquired its iodine content from other sources.

With the exception of the saltpetre deposits of Chile—the main source of the world's production of iodine (about 70 per cent of the total)—no analytical data are available for terrestrial salt deposits, except for chlorine. In the Chile saltpetre, iodine amounts to about 1/35 of the chlorine content, a portion of the iodine occurring as iodate. As an example, we may use an analysis from WETZEL (in STUTZER) of the caliche of Officina Alianza, which contains 470 ppm NaI and 330 ppm $NaIO_3$. The iodine content of this deposit has given rise to much discussion; according to WETZEL it is most probable that an atmospheric source is involved. The perchlorate which, according to GOLDSCHMIDT (1954), may make up 0·5–6 per cent of the deposit, is worthy of notice in this connection. GOLDSCHMIDT suggests that the ClO_4^- ion may replace the SO_4^{-2} ion. I have not been able to find out anything about bromine and fluorine in these deposits.

As a final summing-up for the sediments, we may mention that KORITNIG calculates the average fluorine content of sediments as 650 ppm F, BEHNE the average chlorine content at 154 ppm Cl, and that of bromine at 3·9 ppm Br. No similar estimate is available for iodine. The available data show, however,

that the iodine content of the sediments, as GOLDSCHMIDT (1938) estimated, is of the order of magnitude 0·8 ppm I.

VIII. METAMORPHIC ROCKS

Concentrations of fluorine due to fluorine-bearing gases liberated by crystallizing granite masses have long been known. These gases percolate, and alter the rocks in the vicinity of the granite, and sometimes the granite itself, giving rise to "greisen." Older examples are given for instance by LINDGREN. In an average mixture of 24 German greisens (VON ENGELHARDT) KORITNIG determined 2·04 per cent F and 0·15 per cent P_2O_5. In a greisen from Zinnwald in the Saxon Erzgebirge, he found a fluorine content of 4·45 per cent F, which is distributed in the rock in the following manner:

	Per cent F
36 weight per cent zinnwaldite with 5·5 per cent F contributes to the rock	1·79
11 weight per cent topaz with 18 per cent F contributes to the rock	2·02
1·35 weight per cent fluorite with 48 per cent F contributes to the rock	0·64
0·07 weight per cent apatite contributes to the rock	0·003
Total	4·453

In a lithionite granite from Eibenstock, Saxony, likewise altered by fluorine, KORITNIG found 1·7 per cent F, which he calculated to be distributed among the minerals of the rock as follows:

	Per cent F
8·0 weight per cent lithia-mica with 5·5 per cent F contributes to the rock	0·44
3·5 weight per cent topaz with 18 per cent F contributes to the rock	0·63
0·15 weight per cent apatite contributes to the rock	0·005
1·29 weight per cent fluorite (by difference) contributes to the rock	0·625
Total	1·70

The measured quantity of fluorite in the rock was 1 per cent. These examples show that in such metasomatic rocks topaz and fluorspar, as well as the micas, play the chief parts as carriers of fluorine.

According to BEHNE's investigations, chlorine and bromine are only present in very small quantities in the same rock. The average mixture of 24 greisens contained 50 ppm Cl and 1·7 ppm Br. BEHNE found 70 ppm Cl and 9·5 ppm Br in the lithionite granite of Eibenstock.

Fluorine and chlorine also occur in limestones involved in skarn formation. I quote a few figures from the collection of analyses made by LARSSON of materials from the Persberg deposit in Sweden, which has been discussed, for example, by LINDGREN. A tremolite skarn contained 4000 ppm F, actinolite-pyroxene skarn 400 ppm F, talc-skarn 4700 ppm F, and mica-chlorite-skarn 12,100 ppm F. 0·86 per cent CaF_2 (= 4200 ppm F) and 500 ppm Cl were found in an amphibole-skarn from Yxsiöfjeld, Sweden. In this case the fluorine is partly present in fluorite, while some is also present in mica and hornblende. KURODA and SANDELL quote from KRUTOW the extraordinarily high figure of 72,400 ppm Cl in a Dashkesanite-amphibole from a Transcaucasian skarn. Chlorine, as already mentioned (see page 188) may be present in scapolite

minerals, which are not abundant in skarns; besides, it is very likely to be removed as the very easily soluble $CaCl_2$. Scapolitization does, however, take place, sometimes in limestones, sometimes in silicate rocks. V. M. GOLDSCHMIDT (1911) gives analyses with 17,800 and 10,100 ppm Cl in scapolites from Aarvold, Norway. Chlor-apatite also occurs abundantly along with scapolite.

Chlorine and fluorine may also be concentrated in other contact minerals; for example GOLDSCHMIDT (1911) quotes old analyses of the vesuvianite from Hamrefjeld, Norway showing 13,500 and 19,700 ppm F. In this mineral also, the formula for which may be written $Ca_{10}(Mg,Fe)_2Al_4[(OH)_4(SiO_4)_5(Si_2O_7)_2]$, fluorine replaces the OH^- ion. In the pyroxenes of the Tiree marble of the Hebrides, HALLIMOND was able to detect traces only of fluorine and chlorine. The fluorine and chlorine contents of an amphibole and a biotite from a gneissic inclusion in the marble are given in Table 29, together with BUDDINGTON's analyses of hornblendes from a gabbro which has been reconstituted to an amphibolite gneiss; the high halogen content of these latter may have been derived from granitic magma.

Table 29. Fluorine and Chlorine Contents of Metamorphic Hornblendes and Biotite (in ppm)

	Hornblendes from amphibolite-gneisses, N.W. Adirondacks (BUDDINGTON, 1952)				From gneissic inclusion in Tiree marble (HALLIMOND)	
	1	5	7	9	Amphibole	Biotite
F	9,100	10,700	1,100	800	1,600	2,000
Cl	300	—	400	6,300	4,600	3,000

Two out of the 10 hornblendes analysed for fluorine, Nos. 1 and 5, show very high results, while of the 3 analysed for chlorine, No. 9 shows a high value. We are dealing with alkali amphiboles, whose contents of Na_2O lie between 1·20 and 2·53 per cent, and of K_2O between 0·61 and 1·49 per cent, but there seems to be no connection between the halogen content and the content of Na_2O or K_2O, or to the sum of these oxides. HALLIMOND's amphibole contains 1·42 per cent Na_2O and 2·60 per cent K_2O.

Other hornblendes, from the north-western Adirondack region investigated by BUDDINGTON, also have high halogen contents. These occur in gneisses which, according to BUDDINGTON (1948), had their origin in "granites" of magmatic formation. They are quoted here because of the description "gneiss." Some of BUDDINGTON's (1953) figures are quoted in Table 30. Further, two hornblendes, in rocks described as granite, will be found in Table 7.

Of other metamorphic rock minerals, SERAPHIM has found 350 ppm F in a chiastolite from Lancaster, Mass., in others the fluorine content was below the detection limit of 200 ppm. At the same time he could find fluorine neither in sillimanites nor in kyanites, epidotes, clinochlore or prochlorite. He found an average of 1300 ppm F in a chlorite from mica-chlorite-schist from Cavendish, Vt. In a chlorite from a pegmatite from Varala, LOKKA found 600 ppm F.

Table 30. Halogen Contents of Hornblendes from Granitic Gneisses of the N.W. Adirondacks (after BUDDINGTON, 1953)

	Fermaghastingsite		Ferrohastingsite		
F	12,900	11,700	9,500	7,200	6,100
Cl	5,800	6,000	7,700	2,600	5,300

Among the rarer fluorine-bearing minerals of metamorphic rocks, mention may be made of the humite group, which were the subject of a monograph by SAHAMA (1953).

I only know of two systematic investigations of the variation in halogen content with respect to distance from a contact: these are the examination of the Rapakivi contact at Ihovaara, Finland (SAHAMA, 1948), and SERAPHIM's work on the behaviour of fluorine. SAHAMA's results are quoted in Table 31.

Table 31. Fluorine and Phosphate Contents at the Rapakivi Granite Contact of Ihovaara, in ppm (after SAHAMA)

	"Normal" Rapakivi granite	Contaminated Rapakivi from the contact	Mica gneiss fragment in Rapakivi	Mica gneiss from the immediate vicinity of the Rapakivi contact	Mica gneiss about 1 km E. of Ihovaara hill
P_2O_5	1,300	1,200	2,100	1,800	2,700
F	400	500	2,500	300	300

Only in the inclusion of mica gneiss has a notable enrichment in fluorine been detected, even so it does not approach the fluorine content of the standard mixture of the Rapakivi granite (see Table 3). Indeed, no addition of fluorine is to be found in the immediate neighbourhood of the contact.

SERAPHIM investigated an inclusion of an argillaceous Cambridge siltstone in the Quincy granite of Massachusetts, and found the fluorine distributed as shown in Fig. 3.

The fluorine content, plotted on a logarithmic scale, is seen to decrease sharply at the granite margin, then rise very rapidly in the siltstone. Mafic constituents, the main carriers of fluorine, are wanting in the marginal zone of the granite. In the other contacts examined by SERAPHIM, too, he was able to establish that the fluorine had migrated only over distances of a few inches. The fluorine-rich zone was usually to be recognized by the presence of amphiboles. It thus appears that in these cases fluorine has migrated along with other elements such as iron and magnesium, so that conditions were very different from those obtaining in greisen formation.

Finally, mention may be made of some work by GILLULY. Examining the silicified ores of Ophir Hill (Stockton and Fairfield quadrangles of Utah), he calculated that 3×10^6 kg fluorine were introduced into a limestone of 3×10^6 square feet in extent and 60 feet in thickness, together with 900×10^6 kg SiO_2,

270×10^6 kg Al_2O_3, 10×10^6 kg Na_2O, 160×10^6 kg K_2O, 9×10^6 kg P_2O_5 and Ca, S, FeS_2, PbS, ZnS totalling 797×10^6 kg. GILLULY considers that he is here dealing with hydrothermal solutions of an alkaline nature. These relative proportions themselves show that SiF_4 was not involved in this particular case. Since about 90 per cent of the original limestone consisted of $CaCO_3$, the content of fluorine compounds in the replacing solutions cannot have been very high, on account of the insolubility of CaF_2.

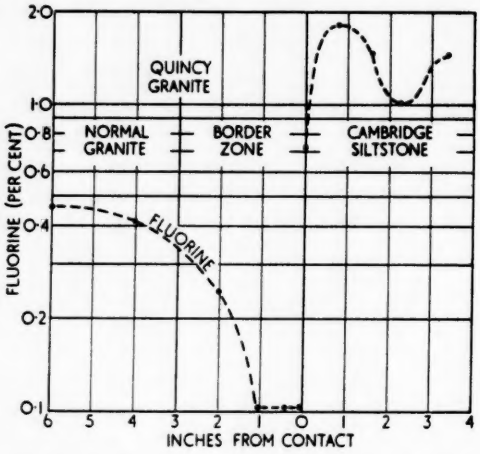

FIG. 3. Behaviour of fluorine at a granite contact (after SERAPHIM).

IX. BALANCE

The question of how a balance in the natural economy of the elements may be achieved is still absolutely open. In 1948 I tried to show that GOLDSCHMIDT's attempt was correct, at least in so far as order of magnitude is concerned, and provided one agreed with his general assumptions. I am aware indeed that these assumptions may be questioned, but this is not the place to enter into a discussion of them. Therefore I shall only give here a synopsis in Table 32, which is

Table 32. Geochemical Balance of the Halogens (referred to 1 sq. cm of the Earth's Surface)

Element	In eruptive rocks, kg/cm²	In sediments, kg/cm²	In sea water, kg/cm²	Percentage of eruptive rock content in the oceans
F	$1{\cdot}12 \cdot 10^{-1}$	$1{\cdot}1 \cdot 10^{-1}$	$3{\cdot}9 \cdot 10^{-4}$	0·35
Cl	$2{\cdot}4 \cdot 10^{-2}$	$2{\cdot}6 \cdot 10^{-2}$	5·4	22,500
Br	$4{\cdot}95 \cdot 10^{-4}$	$6{\cdot}6 \cdot 10^{-4}$	$1{\cdot}8 \cdot 10^{-2}$	3,630
I	$4{\cdot}8 \cdot 10^{-5}$	$1{\cdot}35 \cdot 10^{-4}$	$1{\cdot}4 \cdot 10^{-5}$	29·2

based upon GOLDSCHMIDT's calculations, using 160 kg/sq. cm for the proportion of magmatic rocks, 170 kg/sq. cm for the sediments, and 278·72 kg/sq. cm for the oceans; together with the average values already given in the text for fluorine by KORITNIG, for chlorine and bromine by BEHNE, and for iodine by GOLDSCHMIDT. Despite all remaining uncertainties, the table shows quite well that fluorine essentially originates from the magmatic rocks, while iodine, bromine and chlorine must be considered to be supplied as products of the volatile phase of magma, unless one is willing to postulate that the primitive oceans or the primitive atmosphere of the earth were especially rich in halogens.

SUMMARY

The available data concerning the halogen elements in the cosmos and in meteorites are still very uncertain, and in part contradictory.

In the magmatic rocks chlorine and fluorine may either occur in their own mineral phases, such as apatite (and, as a post-magmatic mineral, fluorite), or they may replace OH^- ions in other minerals, especially micas and amphiboles. In addition, the O^{2-} ion in sphene may be partly replaced by F^-. It appears that fluorine is first of all incorporated into apatite, any excess entering mica, hornblende and sphene. Chlorine is mainly incorporated in micas and hornblendes. Part of the halogens may be present in aqueous solutions or gases in mineral inclusions, or dissolved in solid rock glasses.

There seems to me to be no certain correlation between halogen content and the chemical composition of a rock. Neither is the mode of crystallization—plutonic or effusive—always a decisive factor. These two halogens (F and Cl) are thus particularly appropriate to demonstrate the fact—rather disregarded in many geochemical works—that the abundance of an element also depends upon its supply at the place in question. The halogens show this particularly well, because they are more readily transportable in the form of volatile compounds than are many other elements. Evidently, conditions obtaining prior to the consolidation of a magmatic rock—e.g. partial degassing—may decisively influence their relative proportions.

Among post-magmatic processes, the contribution made to the halogen contents of the atmosphere and hydrosphere by volcanic exhalations is of importance in general geochemistry. Bromine and iodine occur in much the same proportions in magmatic and post-magmatic products: in rocks and minerals I $\sim$ 1/10–4/100 Br. In weathering processes, halogens are released to the soil and to the hydro- and biospheres. The behaviour of fluorine in the soil depends upon the kind of weathering—i.e. upon the breakdown of fluorine-bearing minerals, and perhaps possible combination with phosphoric acid. Chlorine is easily removed, but may be returned in rain water. Bromine is concentrated in organic matter. In the uppermost soil horizons iodine is concentrated from the air or from rain water, and to some extent by the agency of organisms.

In the hydrosphere, fluorine is important from a medical point of view; more than 1·2 ppm F in drinking water gives rise to disease, while too little, on the contrary, promotes dental caries. Compared with river water, all the halogens are enriched in sea water—fluorine the least, bromine the most. From the oceans the halogens find their way in rain back to the land areas

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("cyclic salts"). In recent marine sediments the ratio $Cl:SO_4$ is raised when SO_4 is used up by reduction processes, and lowered when Cl is incorporated into clay minerals.

The combination of fluorine with phosphorus is especially pronounced in the biosphere. The element is concentrated only in vertebrate bones and teeth and in the phosphate-rich shells of brachiopods. For the rest, the contents of fluorine fall below the average in rocks. In living matter, chlorine is present to the extent of 100–1000 ppm; its occurrence in coals needs more precise investigation. Bromine and iodine may be concentrated in organisms; for this reason they are found in the saline waters accompanying crude petroleum.

Coarse clastic sediments contain less than average amounts of fluorine and chlorine, while bromine and iodine are about the same as the averages in igneous rocks. Because of the presence of clay minerals, the pelites may contain larger quantities of fluorine and smaller quantities of chlorine. Bromine is present in rather larger amounts in clays which are rich in organic matter. In ordinary clays also the ratio Cl:Br is displaced in favour of bromine. The iodine content, too, increases with content of organic matter.

In limestones a substantial proportion of the fluorine is present in admixed clay material, or combined in phosphate, and accordingly is small in amount. Unleachable chlorine is similarly present, generally in small quantity, in part probably in fluid inclusions. The bromine and iodine contents of these rocks result from the remains of organisms buried in the sediments. Similar considerations apply to the siliceous rocks. In the iron ores relatively small amounts of fluorine, and indeed of chlorine also, are combined with phosphate, while bromine and iodine are controlled by organic matter. High proportions of fluorine are encountered in phosphate deposits. If the ratio $F:P_2O_5$ exceeds that of the formula for fluor-apatite, the possibility of sulphate- or carbonate-bearing apatites must be borne in mind. The phosphates contain relatively large proportions of iodine, up to 280 ppm.

In the evaporites, fluorine is essentially found in anhydrite, with which it is precipitated on evaporation. Bromine enters by isomorphous substitution into potash salts. The data for iodine deviate somewhat; in general it will remain behind in the residual liquors. Among terrestrial salt deposits, the high iodine contents of the Chile saltpetre is worthy of note.

Among metamorphic rocks may be mentioned the fluorine-rich greisen, in which topaz and fluorite occur, but in which very little chlorine is found; and also skarn formation, where an enrichment of chlorine in amphiboles may be noted. Scapolitization may also give rise to high chlorine contents. Apart from greisen formation, the examples so far studied indicate that the effects of fluorine-bearing fluids are restricted to a few inches from a contact.

Especially in the field of metamorphism much work still needs to be done on the geochemistry of the halogens. In the case of the other rocks, too, the quantity of available data must not blind us to the fact that our knowledge is still very fragmentary. That is also true of the geochemical balance of these elements, which indicates from our present knowledge that fluorine may have its source in the magmatic rocks, while chlorine, bromine, and iodine on the other hand may be derived from volcanic exhalations or from a hypothetical primitive ocean.

Because of the limited space at my disposal, I have considered it best to

restrict myself to the presentation of facts, and especially of new data, and to resist as far as possible the temptation to make theoretical deductions or forecasts.

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GEOCHEMISTRY IN THE U.S.S.R. (1948–1953)

By S. I. TOMKEIEFF

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INTRODUCTION

THE U.S.S.R. with its vast area and its equally vast population might well be expected to have much to contribute to the science of geochemistry and to other sciences. In geochemistry, however, Russia has more than a proportionate share in modern development. It has a tradition and an inspiration dating from the very beginning of the science. D. I. MENDELEIEFF (1834–1907) the discoverer of the periodic law, is well known to all chemists of whatever branch, but more particularly important for geochemistry is his contemporary V. V. DOKUCHAEV (1846–1903), founder of modern Russian school of soil science and teacher of three very prominent men, who in their different spheres, themselves applied and handed on to their own pupils, his method of chemical and genetic approach to problems: K.D. GLINKA (1867–1927) was DOKUCHAEV's successor as a pedologist, F. Y. LOEWINSON-LESSING (1861–1939) was one of the greatest Russian petrologists and finally V. I. VERNADSKY (1863–1945) was both a great mineralogist and the actual founder of the Russian school of geochemistry. He, in his turn, inspired his pupil A. E. FERSMAN (1883–1945), who gave his first course of lectures on geochemistry in Shanyavsky Free University in Moscow in 1912. The two men, VERNADSKY and FERSMAN, were very different in temperament. VERNADSKY first defined geochemistry as the "study of chemical elements in the earth's crust" as distinguished from mineralogy "which studies natural chemical compounds—the minerals" (VERNADSKY 1922). Minerals, he held, were only temporary phases of a continuous process and geochemistry, embracing in fact genetic mineralogy and genetic petrology, had a wider and deeper significance than mere descriptive mineralogy or systematic petrology. The biosphere, (plants and animals) according to VERNADSKY, was also a powerful agent of transformation, as well as a geochemical medium, and in a sense VERNADSKY may be called the founder of a new science-biogeochemistry

(VERNADSKY, 1929). He was also very much interested in radioactivity and in 1915 he was the founder and the first director of the Radium Institute in Russia. VERNADSKY's two books in French—*La Géochimie* (1924) and *La Biosphere* (1929)—brought his work within the reach of the scientist who knows no Russian. The first book is and is likely to remain a classic of geochemistry.

FERSMAN was a different proposition. A great traveller, he approached the subject from the angle of regional mineralogy or "topomineralogy" as he called it. Rather optimistically FERSMAN embarked on an ambitious scheme of writing up the geochemistry of Russia, but only the first issue of this work was published (1922). In this book he tried to define the principle of geochemistry. First of all he laid stress on the genetic aspect of the science of mineralogy and on the need to interpret minerals from the standpoint of the chemical elements. The paragenetic association of minerals leads to genetic interpretation and this in turn leads to a wider concept of the geochemical migration of elements and geochemical cycles. These cycles and their environment, both material and energetic, determine genetic types. Final explanation must be sought in the energetic aspects of atom-elements and thus be based on the periodic table of the elements. This book was soon followed by another (1923) in which FERSMAN linked up geochemistry on one side with atomistics and, on the other, with geospheres and cosmochemistry.

Meanwhile the progress in atomistics and structural crystallography during the decade 1920–30 opened up a new vista in science and had a tremendous repercussion of geochemistry. This new geochemistry, the creation of GOLDSCHMIDT, NIGGLI and FERSMAN, was a different science from the geochemistry of CLARKE and VERNADSKY, the main difference being that it was provided with, or an attempt was made to provide it with, a foundation constructed in the domain of microphysics. First in a series of papers, then in a monumental "*Geochemistry*" (1934–39), FERSMAN, presented this new science as a vista stretching from the atom with its whirling electrons to the cosmos as a whole. All the details previously known to mineralogists and petrologists were fitted neatly into this unified scheme. Energetics was appealed to provide the cement and individual phenomena were presented as ripples on this whirl of cycles and sub-cycles. This book, with data culled from all possible sources and crammed full of references, introducing new ideas and new terms, seems to us now a large but rather confused edifice. In any case this and other work by FERSMAN remains untranslated. Shorter and handier books on geochemistry have since been published by SHCHERBINA (1939) and SAUKOV (1951), and it is as a guide to these and other books and articles published in the U.S.S.R. that the present article is intended.

Its scope is to present in as brief a form as possible the main advances made in the U.S.S.R. during the last six years (1948–53) in the field of geochemistry, chemical mineralogy, chemical petrology and allied sciences. Only highlights have been indicated. Considering the number of active scientific institutions and scientific and technical periodicals in the U.S.S.R., a complete review of the annual achievement in the science of the chemistry of the earth (including technical petrology, physical chemistry, pedology, hydrology, biochemistry) would, at a modest estimate, comprise some one thousand references to papers and books for each year. In the present review this has been cut down to an average of 110 references per year. These references are culled mainly from

three leading periodicals: *Compt. Rend.* (*Doklady*) *Acad. Sci. U.S.S.R.*, *Bull.* (*Izvestia*) *Acad. Sci. U.S.S.R., Sér. Géol.*, and *Mem.* (*Zapiski*) *All-Union Miner. Soc.* and the most important books. One of the difficulties in preparing this review has been the difficulty of obtaining the necessary literature in this country. For example I have been unable to find the "*Izvestia*" and the "*Zapisky*" for 1948 in any library in London. For workers using the review the language difficulty arises. It is impossible here to give more than very brief accounts of the contents of the more significant papers and in general the contents of books can be indicated only by these titles. This means that scientists interested in a subject must consult the original publication, and this, in accordance with present Russian policy will be in Russian or some other language of the Union and will have no translation or abstract in a Western European language. A certain number of Russian papers are abstracted in the *Chemical Abstracts* (English and American editions) and in the *Mineralogical Abstracts* (published by the Mineralogical Society of London). A few reviews bearing on the progress of geochemistry and geology in the U.S.S.R. have been published in *Nature* (1944, *154*, 582, 711, 814; 1945, *156*, 607, 640, 759; 1946, *157*, 239, 310, 378; 1946, *158*, 31, 315; 1947, *160*, 846). An article on the "Sources of Russian scientific information" has been published by A. L. MACKAY in *Aslib Proceedings*, 1954, 6(No. 2), but he does not deal specifically with the geological and geochemical publications.

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The present review is divided into six sections and is based on some 700 references.

I. GEOCHEMISTRY, GEOSPHERES, ELEMENTS

1. *The Science of Geochemistry*

The principles of geochemistry are discussed by BETEKHTIN (1952), who accepts the atomistic groundwork as the foundation of geochemistry and at the same time emphasises the practical aim of geochemistry namely to elucidate the probable genesis of minerals and ores. According to him the fundamental law of geochemistry is as follows: "The occurrence of the chemical elements in the earth's crust depends on their atomic structure". BETEKHTIN is supported but also criticised by LEBEDEV (1953) who warns geochemists against undue preoccupation with cosmochemistry, while, on the other hand VOITKEVICH (1953) considers that geochemistry must be linked with cosmochemistry. He writes "Radioactivity of the earth's crust must therefore be considered as a cosmic phenomenon, historically inherited by terrestrial matter and determining the main trend of the geological history of the earth, where the cosmic and terrestrial geological phenomena are so closely interelated that they cannot easily be separated. The transformation of the solar energy manifests itself in the exogenic geological processes. The energy of radioactive disintegration, in its historical aspect and also considered logically, must be the leading factor of the endogenic geological processes. The earth is an inseparable part of the cosmos, part of the cosmic cycle of atoms, which includes the processes of their synthesis and disintegration". (p. 32). BOGANIK (1953), in his general review of nuclear geochemistry, also expresses a desire to see nuclear chemistry as the foundation of geochemistry. SHCHERBINA (1952), taking as an example the diagonal series Ti—Nb—W of the periodic table, discusses the relation between the extranuclear structure of the atom and its geochemical properties.

2. *Geospheres and the Distribution of the elements*

BUBLEINIKOV, in a popular book (1951), discusses the modern views of the earth's structure, MAXIMOVICH (1950) discusses geodynamic zones as a background for geochemical and geological processes. These zones are as follows: geotectonic, structural, climatic, geomorphological, and the penosphere (the zone of human activity). According to MAXIMOVICH (1948), an important factor of geospheres is their porosity, the averages of which he calculates. The problem of porosity is connected with the compaction of sediments, especially as related to orogenesis, a problem discussed by RONOV (1948). The problem of geochemical types in relation to orogenesis is discussed by BILIBIN (1950).

SHCHERBINA (1949; 1950) discusses the concentration and the dispersion of the elements in the earth's crust as resulting from oxidation and reducing processes, while KAPUSTINSKY (1952) is interested in the distribution of the elements in relation to their atomic volumes, and on the basis of the atomic volumes curve, which takes the form of a series of parabolas. The distribution of cobalt in the earth's crust is discussed by MALYUGA (1952) and of fluorine in soils by VINOGRADOV and DANILOVA (1948).

3. *Radioactive Elements and the Age of the Earth*

The last few years have been marked by the appearance of several popular books on this subject published by SHCHEPOTIEVA (1951a and b), BATAEV (1951) SHEVLYAKOV (1951), and by a second edition of BRESLER's book (1952). The leading authority on radioactivity is still V. I. KHLOPIN, (born in 1890, died in 1950). He began work on radioactivity with V. I. VERNADSKY in 1915, becoming in 1922 the assistant director, and in 1937 the director of the Radium Institute.

KHLOPIN and GERLING (1948) applied their formula for the determination of the age of uranium minerals. The formula is as follows:

$$t = \frac{1}{\lambda_\alpha} 2{\cdot}30 \log_{10} \left[\frac{Xe}{0{\cdot}14 N_1 (\lambda_\Delta / \lambda_\alpha)} + 1 \right]$$

in which: $\lambda_\alpha = 1{\cdot}54 \times 10^{-10}$ per annum, constant of disintegration of U, $\lambda_\Delta = 5{\cdot}1 \times 10^{-17}$ per annum, another constant, Xe = atomic clarke of xenon, N_1 atomic clarke of uranium, t = geological age of the mineral.

According to their calculations, the age of the earth's crust is 2×10^9 years. The evolution of krypton is five to six times less than that of xenon and certain amounts of xenon and krypton are derived from thorium. It is suggested that helium was occluded by the terrestrial material from the primary gas, while argon is a product of nuclear processes.

KHLOPIN (1949a, b) criticizes HAHN's hypothesis of transformation of Be^8 into $2He^4$, because of the presence in the radioactive minerals of a small amount of He^3. Beryllium, boron and lithium minerals contain a large amount of helium, occluded during their magmatic crystallization.

GERLING and others (1949) found that K^{40} is not only an β-emitter but can also give rise to A^{40} through K-capture, the constant of distintegration of which is thirty times smaller than the one found by other workers. On condition that A^{40} is not lost the constant is $(6{\cdot}1 \pm 1{\cdot}2) \times 10^{-11}$ years^{-1} and A^{40}/K^{40} increases with the age of the mineral.

CHERDYNTZEV and KOZAK (1949) found that a certain amount of helium in minerals is not of radioactive origin but occluded by them during their primary

crystallization. Thus magnetite from a recent lava of a KAMCHATKA volcano, according to its helium content ($2{\cdot}6 \times 10^{-5}$ cm^3/g) should be 500 million years old.

VOITKEVICH (1950) discusses the radioactivity of K^{40} which through β-emission is transformed into Ca^{40} and through K-capture, into A^{40}. The thermal regime of the earth as due to the radioactivity of the four elements can be calculated as follows:

Table I. Heat Evolved in Calorie per Hour

	Present time	2×10^9 years ago	3×10^9 years ago	4×10^9 years ago
Uranium	$21{\cdot}26 \times 10^{16}$	$29{\cdot}42 \times 10^{16}$	$34{\cdot}06 \times 10^{16}$	$39{\cdot}03 \times 10^{16}$
Actinouranium	$0{\cdot}89 \times 10^{16}$	$6{\cdot}33 \times 10^{16}$	$17{\cdot}34 \times 10^{16}$	$43{\cdot}43 \times 10^{16}$
Thorium	$20{\cdot}27 \times 10^{16}$	$22{\cdot}78 \times 10^{16}$	$24{\cdot}12 \times 10^{16}$	$25{\cdot}13 \times 10^{16}$
Potassium	$4{\cdot}70 \times 10^{16}$	$19{\cdot}46 \times 10^{16}$	$39{\cdot}53 \times 10^{16}$	$80{\cdot}42 \times 10^{16}$
	$47{\cdot}12 \times 10^{16}$	$77{\cdot}69 \times 10^{16}$	$115{\cdot}05 \times 10^{16}$	$188{\cdot}09 \times 10^{16}$

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In his review of the data relating to the determination of the age of the earth, VOITKEVICH (1951) gives the range of $3{\cdot}3 \times 10^9$ to 5×10^9 years. On the other hand BOGANIK (1951) criticizes the concept of a constant rate of radioactive disintegration and suggests that it is influenced by external conditions. VINOGRADOV and others (1952), after a study by a mass spectrograph method of thirty-two samples of galena of various ages, conclude that much of the previous work is not satisfactory because of the factor of redistribution of uranium, thorium and lead during the formation of the geospheres. For the age of the earth they give the range $2{\cdot}1 \times 10^9$ to 5×10^9 years.

GERLING and others (1952) give an account of the first application of the argon method for the determination of the age of minerals. Nine minerals, in age ranging from Archaean to Jurassic, gave results in good agreement with the helium and lead methods. The argon method, however, has still to be perfected and the constants of K-decay and β-decay more accurately determined.

BURKSER (1950) presents a review of the age determination of meteorites. Forty-three iron meteorites show a range from less 0·11 to 6800 million years. GERLING and PAVLOVA (1951) have applied the argon method to the age determination of two stony meteorites, $3{\cdot}03$ and $3{\cdot}00 \times 10^9$ years respectively, and this work was further extended by GERLING and RIK (1952), results of which are given in the table below:

Table II

Name of meteorite	Kg/g	K^{40} g/g	Ar g/g	Ar/K	Age 10^6 years
Kunashak	0·00066	$7{\cdot}9 \times 10^{-8}$	$4{\cdot}3 \times 10^{-9}$	0·054	720 ± 250
Pervomaisky	0·00081	$9{\cdot}6 \times 10^{-8}$	$4{\cdot}5 \times 10^{-9}$	0·045	640 ± 250
Sevrukovo	0·00086	$1{\cdot}03 \times 10^{-7}$	$3{\cdot}1 \times 10^{-8}$	0·30	2400 ± 250
Zhovtnevyi	0·0018	$2{\cdot}16 \times 10^{-7}$	$1{\cdot}02 \times 10^{-7}$	0·474	3030 ± 100
Saratov	0·0017	$2{\cdot}04 \times 10^{-7}$	$9{\cdot}54 \times 10^{-8}$	0·468	3000 ± 100

As applied to tectites by GERLING and YASHCHENKO (1952) the argon method gave the following results:

Table III

	K%	K^{40}%	Ar c.c./g	Ar/K^{40}	Age, years
Rizalite	0·0171	$2·0 \times 10^{-6}$	$8·0 \times 10^{-7}$	$7·2 \times 10^{-4}$	$< 1·2 \times 10^{7}$
Indochinite	0·0228	$2·7 \times 10^{-6}$	$3·8 \times 10^{-7}$	$2·6 \times 10^{-4}$	$< 4·6 \times 10^{6}$
Moldavite	0·0314	$3·8 \times 10^{-6}$	$4·2 \times 10^{-7}$	$2·1 \times 10^{-4}$	$< 3·1 \times 10^{6}$

It is suggested, therefore that tectites are not of cosmic origin.

4. *Isotopes*

An important review of non-radiogenic isotopes in geology, in which a number of Russian works is discussed, has been published by EARL INGERSON (*Bull. Geol. Soc. Amer.*, 1953, **64**, 301 to 374) and RANKAMA (1954).

(a) *Oxygen*—DONTZOVA (1948; 1952), by oxidizing iron in the presence of normal water, atmospheric oxygen water and oxygen-enriched in O^{18} water, proved that the greater part of the oxidation of iron is produced by oxygen derived from water. By removing water of crystallization from iron hydroxide minerals, DONTZOVA (1950) found that in brown iron ore and in hydrogoethite, the water shows densities near normal ($-0·5\gamma$ to $+0·8\gamma$) [$1\gamma = 1 \times 10^{-6}d$; d density of water at 3·98°C]. In magnetite from the limestone contact zone water averaged $5·0\gamma$ heavier than normal water, while water from the oxygen of the limestone was $7·5\gamma$ heavier. VINOGRADOV and DONTZOVA (1952) made a further study of the oxygen isotopes from the contact-metamorphic minerals (1952) and by passing $FeCl_2$ and $FeCl_3$ vapour through crushed limestone at temperatures of 200 to 750°C they produced magnetite. In this case the density obtained ($+7·5\gamma$) was similar to that of the limestone. Thus this method makes possible differentiation between minerals of sedimentary and minerals of contact-metamorphic origin, because the contact-metamorphic (skarn) minerals are on the whole richer in O^{18}. TANATAR (1952) has also confirmed that iron ore minerals of different genetic types have different oxygen isotopes concentration.

TEIS (1950a, b) found that water prepared from the oxygen of CO_2, cotton wool and glucose gave 11γ, 10 to $10·7\gamma$ and 10·1 to $11·2\gamma$ respectively, that prepared from the oxygen of stalactite, salt-lake limestone and marine limestone (1950a) gave $6·8\gamma$, $7·0\gamma$ and $8·1\gamma$ respectively and that prepared from hot springs carbonate minerals 2·5 to $4·0\gamma$. TEIS (1951) therefore concluded that the isotope method is most suitable for the determination of the temperature of formation of carbonates. This, however, is disputed by KARPACHEVA and ROZEN (1953) who think that the "UREY-NIER geological thermometer" which provides for the determination of the temperature of the ancient oceans at their formation by the determination of O^{18} in limestones deposited in them, is not valid, because the isotopic content is affected by the isotope exchange which occurs at room temperature between the limestone and the water.

This contention is supported by numerous laboratory experiments carried out by these two authors (KARPACHEVA and ROZEN, 1949; 1950a, b; 1951).

(b) *Carbon*—TROFIMOV (1950a, b) has determined the ranges of C^{12}/C^{13} ratio in meteorites and rocks, as summarized in the table below:

Table IV. C^{12}/C^{13} *Ratio*

	Range	Average	C%
In 26 stony meteorites	88·9–90·9	90·61	0·017–2·65
In 13 iron meteorites	89·6–91·8	90·68	0·011–0·43

In a later paper TROFIMOV (1952) gave the following C^{12}/C^{13} averages:

Table V. C^{12}/C^{13} *Averages*

Calcareous rocks	90·0
Meteorites	91·95
Igneous rocks	92·1
Asphalts and asphaltites	92·2
Petroleum	93·2

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(c) *Sulphur*—For the sulphur isotopes TROFIMOV (1949) gave the following values for the average ratios:

Table VI

Average ratios	S^{34} : S^{33} : S^{32}
Meteorites (2 stone, 2 iron)	4·55 : 0·79 : 100
Sea water, pyrite, volcanic sulphur	4·57 : 0·80 : 100

5. *Meteorites*

A very large amount of work on meteorites is going on in the U.S.S.R. and a good proportion of the published material is abstracted in the Mineralogical Abstracts.

A detailed description of ninety-eight meteorites in the collection of the Academy of Sciences and other museums in the U.S.S.R. has been given by ZAVARITZKY and KVASHA (1952). Each meteorite is provided with a complete record of data, including a chemical analysis if such exists. KRINOV (1948; 1952) has published two books on meteorites and FESENKOV (1948; 1952) has discussed the origin of meteorites. CHIRVINSKY (1948), the veteran Russian petrologist, gives the clarkes of sulphur in iron meteorites as 0·10 per cent and in palassites 0·06 to 0·09 per cent. In another paper CHIRVINSKY (1951) gave a calculated chemical composition of a stony meteorite "Saratov" and in another paper (1949) he discussed the average composition of meteorites and its relation to the periodic table.

VYALOV (1949) gave a chemical analysis of metal (meteorite?) found at Armanty, Outer Mongolia, namely Fe 89·65, Ni 9·92, and small amount of Co, Cu, P, Sr and Si.

YAVNEL (1950) presented the results of a spectroscopic analysis of the constituent parts of the Sikhote-Alin meteorite, namely kamacite, fused crust, schreibersite, troilite and chromite. The bulk composition of this meteorite is given by Fesenkov (1951) as Fe 94, Ni 5·4, Co 0·16, with traces of Hg, Rh, Pd, Ag, Pt and Au. YUDIN (1952) gave a chemical analysis of the stony meteorite (olivine chondrite) of Kunashak, Urals. DODIN (1952) gave a chemical analysis of a probable meteoritic iron from Tuva, Upper Enisey region—Fe 83, Ni 16·37,

Co 0·52. YUDIN (1952) described a chondrite from Vengerovo, Novosibirsk district, containing grains of native copper embedded between nickel-iron and troilite.

6. *Crystal Structure*

An extensive review by A. L. MACKAY—"Recent Soviet work in the field of crystallography" Supplement to Nuovo Cimento, 1953, No. 4," 10,378–414, covers the whole field of crystallography and contains over 300 references. In the present review only recent work dealing with natural minerals is discussed.

KITAIGORDSKY (1950; 1951) provides text books on X-ray analysis, PINSKER (1949; 1953) on electronography (electron diffraction) and BELOV (1947; 1951) on structural crystallography and structural mineralogy. BELOV (1949a and b) discusses new structural types among silicates and other minerals, the crystal chemistry of mineralisers (1950; 1951) in terms of ionic radii and structural replacements, the crystallization of the silicates and its relation to the reaction series and the influence of (OH) and F ions.

ZHDANOV and RUSAKOV (1952) discuss the isomorphism of anosovite Ti_2TiO_5, Fe_2TiO_5 and Al_2TiO_5. BEUS (1953) discusses the isomorphism of beryllium. The closeness of radii of Be^{2+} and Si^{4+} and also of $[BeO_4]^{6-}$ and $[SiO_4]^{6-}$ explains the heterovalent replacement in silicates. Such a replacement is accompanied by a loss of energy unless combined with a replacement of the type $Mg^{2+} + Si^{4+} \rightarrow Ti^{4+} + B^{2+}$ and the like. One may also postulate the replacement of $[Al_4]^{5-}$ by $[BeO_4]^{6-}$, as for example in beryl and cordierite. Other relations are discussed as well.

SHISHKIN (1950) is interested in the role of oxonium (OH_3), the radius of which (1·35 Å) is close to that of NH_4(1·43 Å) and the possibility that oxonium ion is present in hydrous minerals.

Works dealing with the crystal structure of individual minerals can only be listed without giving the numerical data:

Milarite by BELOV and TARKHOVA (1949) and PASHEVA and TARKHOVA (1953), ramsayite by BELOV and BELYAEV (1949), olivine by BELOV and others (1951), ilvaite by BELOV and MOKEEVA (1951), dioptase by BELOV and others (1952), epidote by BELOV and RUMANOVA (1953), tourmaline by BELOV and BELOVA (1949; 1950).

Electronographic analyses of minerals were done as follows:

Kaolinite by PINSKER (1950), pyrophyllite by ZVIAGIN and PINSKER (1949) and $CoCl_2 . 2H_2O$ by VAINSTEIN (1949).

7. *Energetics*

FERSMAN was the first to emphasize the importance of the energy of the crystal lattice in geochemistry and made a special study of the energy of the crystal lattice of minerals in terms of energy coefficients. LEMMLEIN (1936) has calculated the energy of the crystal lattice of the principal rock-forming silicates as referred to the structural unit (per one atom of Si or Al). He found that this value of energy was decreasing in procession from the early formed minerals to those formed later, as marked on the sequence of reaction series. TAUSON (1949), in a criticism of this work, pointed out that LEMMLEIN had neglected the

oxygen links in the silicates. According to him the stability relations are determined not by the energy of the crystal lattice but by the increasing number of oxygen links as compared with cation links. In a later paper, TAUSON (1950), discussing the energetics of isomorphous replacement in silicates, produces cases of simultaneous replacement of couples of ions, as for example the replacement of $Ca^{2+}Ti^{4+}$ by $Y^{3+}Al^{3+}$ in sphene $CaTiSiO_5$. The relation between the heat of formation and the energy of the crystal lattice of silicates is discussed by LEBEDEV (1952).

In a series of papers LEBEDEV (1946; 1948; 1953) and BELOV (1953) propose a rather unusual hypothesis to explain the origin of the thermal and tectonic energy of the earth in terms of the energy of the crystal lattice. According to LEBEDEV the Al to O distance, on the average, among the surface minerals, such as clay minerals, is 1·9 to 2·1 Å (octahedral co-ordination), while in the case of deep-seated minerals, such as feldspars it is 1·6 to 1·7 Å (tetrahedral co-ordination). It is suggested that the larger Al to O distance is due the action of solar energy, while the decrease of this distance in depth produces a liberation of energy which manifests itself in the form of magmatism and orogenesis. Aluminium is thus considered to be an accumulator of solar energy. Other implications of this hypothesis, such as the possibility of other elements being involved, are also discussed.

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INTRODUCTION AND SECTION I—REFERENCES

All references, unless indicated are in Russian.

Abbreviations:

DOK = *C.R.* (*Doklady*) *Acd. Sci. U.S.S.R.*
IZV = *Bull.* (*Izvestia*) *Acad. Sci. U.S.S.R., Sér. Géol.*
ZAP = *Mem.* (*Zapiski*) *All-Union Miner. Soc.*

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II. MINERALS

1. *Methods*

(a) *Thermal Analysis*—The methods of thermal analysis, developed some fifty years ago by N. V. KURNAKOV and his school, are very largely applied in Russia for the study of minerals and rocks. Improvements of old methods and invention of new methods are constantly going on. Thus BERG and RASSONSKAYA (1950) devised a rapid method of thermal analysis using samples of 20 to 100 mg with time per sample 3 to 10 min. BERG and RASSONSKAYA (1951) also invented a new apparatus for thermal analysis for temperatures up to 900° and pressures up to 15 atm. VITAL (1952) devised a micromethod of thermal analysis by using a crucible provided with a vertical partition and by using a very small sample, placed in the cavity of the neutral substance. Another rapid thermographic method in combination with the use of a torsion balance was devised by TZVETKOV (1951). He used this method for the analysis of carbonates. IVANOVA and TATARSKY (1950) likewise studied carbonates and their mixtures with clay

material by the use of a special method. TZVETKOV (1952) devised a method of quantitative determination of quartz in rocks by means of thermal analysis. SYROMYATNIKOV (1950) invented a new apparatus (exoclave) for the study of minerals at high temperature and high pressure. KELER and KUZNETZOV (1953) invented a special apparatus for a complex analysis of silicates at temperatures up to 1300°C. This apparatus registers simultaneously (1) dilatation of the sample, (2) loss of weight, (3) differential thermal curve and (4) temperature of the furnace. Fibroferrite and melanterite have been studied thermally by TZVETKOV and VALYASHIKHINA (1953).

(b) *Spectrography*—INDICHENKO (1948) found that additional bores in the lower carbon prevent spluttering and loss of material during the analysis of iron and manganese ores. BOROVIK (1950) suggested that lines of molecules SiO, AlO, CaO and CaF can be used for the determination of minerals. BOROVIK (1953) also described a new method for the quantitative determination of alkalies in rocks. ZALMANZON and LIZUNOV (1952) compared the results of spectrographic and chemical analysis of ninety samples of sedimentary material for V, Cr, Cu, Ni and Co, and they found a good measure of agreement between the two methods. WASSERBERG, KASHIRTZEV and POPOVA (1953) have studied the distribution of gallium among the Upper Palaeozoic deposits of Verkhoyansk region by the use of spectroscopic method.

(c) *Varia*—The application of the electron microscope to the study of ore minerals and ore structures was discussed by IVANOV (1951) and SYROMYATNIKOV & FILIMONOV (1953). MALYUGA (1951) described the application of the soil-floristic methods of prospecting for Ni, Cu and Co ores, while RONOV & ERMISHKINA (1953) discussed the method of preparation of quantitative geochemical maps by the superposition of various iso-lines. RONOV and RATYNASKY (1952) provided a formula for the calculation of the average composition of rocks in a stratigraphical column.

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2. *Artificial Minerals*

As shown by LAPIN (1951) experimental mineralogy and technical petrology have been cultivated in Russia for a considerable time. During the last four decades the study of refractories, ceramics, glass, slags and cast basalt has greatly advanced, principally through the efforts of D. S. BELYANKIN (1876–1953) and his school. In 1918 was founded the Experimental Institute of Silicates in Moscow and in 1919 the Ceramic Institute in Leningrad. Subsequently many other similar institutes were established in various towns. The published material relating to the study of high temperature phase equilibrium and artificial melts, as well as the study of solutions, can be found in many and various scientific and technical journals. In the present review only a small number of works of this type is reported.

Recent books published on this subject are those of BELYANKIN, IVANOV and LAPIN (1952), BELYANKIN, LAPIN and TOROPOV (1949) and GINZBERG (1951).

An important controversy arose recently over the classical system Al_2O_3—SiO_2 and the incongruent melting of mullite. TOROPOV and GALAKHOV (1951), using a vacuum microfurnace with a tungsten heater for the study of phase equilibrium of the system alumina-silica, suggested that the formation of corundum, as described in previous works dealing with this system, was due to the evaporation of silica. This evaporation, in their case was prevented by the deposition of a

thin film of metallic tungsten over the sample. Thus they revised the accepted diagram by suggesting that mullite melts without decomposition at 1870°C. On the other hand FILONENKO and LAVROV (1953) through a petrographical study of electro-corundum, found mullite growing on the resorbed corundum. This fact together with a detailed study of the system Na_2O—Al_2O_3—SiO_2, led them to the conclusion that the previously held opinion about the incongruent melting of mullite must be the correct one. On the other hand, however, BUDNIKOV, TRESVYATSKY and KUSHAKOVSKY (1953) on the basis of their thermal, optical and X-ray studies are definitely supporting the view of TOROPOV and GALAKHOV.

MIESSEROV (1952), in his experiments with bentonite and artificial alumino-silicates, concluded that the acidity of the alumino-silicates is due to the exchange ions of aluminium. KURTZEVA (1953) described (optical data and chemical analyses) two iron-rich pyroxenes (ferrosilite) which were found, together with olivine and cristobalite, in a nickel slag. OSTROVSKY (1949) prepared a soda-hydroxile-amphibole. BUDNIKOV and CHEREPANOV (1950), by heating mixtures of BeO and SiO_2 up to 1600°C, failed to obtain phenacite (Be_2SiO_4) unless 2 per cent MnO_2 was added to the mixture. BELYANKIN and LAPIN (1948) discovered cordierite in a technical glass, which, according to them, must have been formed through the contamination of glass with a fragment of refractory material. On the other hand BEREZHNOI and KARYAKIN (1950) produced cordierite in a solid medium by compressing powder mixtures of various oxides and minerals at various temperatures. KARYAKIN and KAINARSKY (1950) described various types of cristobalite (metastable isotropic, scaly, acicular) found in the lining of an acid hearth furnace. KARYAKIN and KAINARSKY (1952) also studied the crystallization of silica from a gas phase. ESIN, GAVRILOV & LEPINSKIKH (1953), by measuring the electromotive force in the Ca—Mg—Al—Si slags at 1470°C, found the presence of the anion Si_4^{4-} and $(SiO_3^{2-})_n$ in the liquid slag. OSTROVSKY (1951) studied the formation of fayalite, aegirine, alkali amphibole and magnetite in the contact zone of marble immersed in a molten mixture of Na-Fe-silicate and water. BELYANKIN and LAPIN (1951) showed the presence of $Ca(OH)_2$ among the powdery weathering products of ferro-vanadium slags. This material, however, in its optical properties was not in agreement with portlandite.

DRUZHININA (1953) obtained artificial crystalline diaspore from a solution of artificial boehmite, "inoculated" by diaspore after 50 hr digestion in an autoclave at 315°C. NIKOLAEV (1952) provided a mathematical thermodynamic theory of the dehydration of brucite-periclase. MCHEDLOV-PETROSYAN (1952) studied the solubility of serpentine after heating, GRUSHKIN and KHELVAS (1951)—the crystallization of quartz from colloidal solutions, KARASIK (1949)—the formation of pseudomorphs in skarns, MOKIEVSKY and MOKIEVSKAYA (1950)—the influence of borax on the crystallization of magnesium sulphate. Finally we have BORNEMAN-STARYNKEVICH (1951) discussing the isomorphous and the non-isomorphous replacements in minerals, and YANULOV (1948) discussing the limits of epitaxial growths of crystals.

3. *Mineralogy Text-Books*

The book by BETEKHTIN (1950) is a capital work on descriptive mineralogy, comparable to DANA's "System". It contains ample and reliable optical, X-ray,

and morphological data, good discussion of such topics as isomorphism, polymorphism, colloidal state and the like. It also provides a clear connection between the physical properties of minerals and their inner structure. The list of minerals described is comprehensive, but the treatment of the genetic-geochemical aspect of mineralogy is inadequate and there are no references. A smaller text-book of mineralogy was published by LAZARENKO (1951) and a text-book on the mineralogy of the silicates by SOBOLEV (1949).

4. *Sulphides, Arsenides, etc.*

MIKHEEV (1949) distinguished three modifications of Cu_3As: α-domeykite (cubic), β-domeykite, artificial (hexagonal) and γ-domeykite (algodonite). GRITZAENKO and others (1953) successfully synthesized vaesite (NiS_2) and polydymite (Ni_3S_4) in an autoclave in a hydrous solution of nickel and iron sulphates. MIROPOLSKY (1951) described the galena which is present in small amounts in limestones and bituminous shales of Devonian age. LAZARENKO (1953) describe brunckite (cryptocrystalline sphalerite) found in the form of white earthy masses in gypsiferous bituminous clays and gave a chemical analysis of this mineral. POLYANIN (1949) describe realgar, probably of biogenic origin, occurring in spherosiderite concretions, fossil plants and fossil fish.

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5. *Halides*

DORFMAN (1950) proposed a new mineral name—belyankite (after D. S. BELYANKIN, and distinct from belyankinite) for a mineral having the composition Al_2O_3 21·88, CaO 34·00, F 49·01, $H_2O +$ 15·35, $H_2O -$ 0·30, less O for F 20·63 = 99·91. FLEISCHER (*Amer. Min.*, 1952, 37, 785–790) and later ERMILOVA and MOLEVA (1953), suggested that sulphur has been missed out and that this mineral is identical with creedite $Ca_3Al_2(SO_4)(F, OH)_{10}\cdot 2H_2O$. GRUSHKIN and PRIKHODKO (1952) discussed the geochemistry and the genetic phases of the fluorides and POKROVSKY (1949) described sal-ammoniac occurring as a sublimate in rock fissures in the vicinity of burning coal.

6. *Oxides*

A new mineral named magnalumoxide was described by BOBKOV and KAZYTZIN (1951). It is a spinel of the composition $(Mg, Fe)_5(Al, Fe)_{18}O_{32}$. GRITZAENKO and others (1950) re-examined a mineral previously named aidyrlite and, on the basis of two new chemical analyses and an X-ray study, concluded that aidyrlite is not a mineral but a mixture of $Ni(OH)_2$, gibbsite and opal. According to IKORNIKOVA (1948a, b) the coloration of brookite is due to iron chromophores and perhaps to the presence of columbite. Ilmenitization of perovskite was discussed by LEBEDEV and RIMSKAYA-KORSAKOVA (1949) who described pervoskite-bearing pyroxenite from KARELIA. The development of secondary ilmenite after perovskite was tentatively attributed by them to the action of hydrothermal solutions. SERDYUCHENKO and MOLEVA (1949) described two spinels from the river Malka in northern Caucasus—a dark green pleonast and a red brown chrome-picotite. The same authors (1953) described spinels from Yakutia in Siberia, providing four chemical analyses and X-ray data. From the same region of the northern Caucasus SERDYUCHENKO described hydromagnesite, $4MgCO_3\cdot Mg(OH)_2\cdot 4H_2O$, as occurring in carbonated serpentine. GERASIMOVSKY and KAZAKOVA (1950) described a new complex oxide or titanate

$2CaO{\cdot}12TiO_2{\cdot}\frac{1}{2}Nb_2O_5{\cdot}ZrO_2{\cdot}SiO_2{\cdot}28H_2O$, a formula based on two chemical analyses and X-ray data. It is found with aegirine and eudialyte in a nepheline-syenite-pegmatite. YURK and RYABOKON (1950) discussed the source of rutile in alluvial deposits of Kiev region which they thought to be mainly of secondary origin, being dehydrated titanium hydroxide derived from sphene and other titanium-bearing minerals found in granite. The chemical constitution and crystalline structure of anosovite (Ti_3O_5) was discussed by RUSAKOV and ZHDANOV (1951) and by BELYANKIN and LAPIN (1951) who suggested the formula $TiO_2{\cdot}Ti_2O_3$ analogous to $TiO_2.Fe_2O_3$. Three analyses of högbomite (Mg, Fe, Mn)$_{11}$·(Al, Fe, Cr)$_{20}$·TiO_{39} and zinc-högbomite were given by MOLEVA and MYASNIKOV (1952).

7. *Carbonates*

Twenty analyses of various carbonates from Kazakhstan were given by SHCHERBINA (1950) who found among them the predominence of dolomite-calcite (gurhofite). The paragenesis of hydrous carbonates found in the serpentinites of Malka river region of northern Caucasus was discussed by YAKHONTOVA (1952). Nickel-bearing calcite from the region of Lake Baikal was described by VLODAVETZ (1948). Ktypeite from Karlovy Vary (Czechoslovakia) was found by ZAVARITZKY and MIKHEEV (1948) to be identical with aragonite.

8. *Phosphates, Arsenates, etc.*

Carbonate-apatites were discussed by BORNEMAN-STARYNKEVICH (1953) and BORNEMAN-STARYNKEVICH and BELOV (1953). Whewellite was described by KALYUZHNY (1948) and SUMIN (1953) who found that although whewellite and fisherite have an identical structure, they are distinct chemical species. Among new phospates are magniophilite (Mn, Fe, Mg)$_3$·$(PO_4)_2$ and mangankoninckite (Fe, Mn)$PO_4{\cdot}3H_2O$ described by BEUS (1950), magniotriplite 4(Fe, Mg, Mn)$_3$·$(PO_4)_2$ 3(Fe, Mg)F_2 described by GINZBURG and others (1951) and kryzhanovskite $MnFe_2(PO_4)_2(OH)_2{\cdot}H_2O$, described by GINZBURG (1950). GINZBURG (1952) also described griphite and GINZBURG and MATIAS (1953) described eosphorite, GINZBURG and VORONKOVA (1950)—oxichildrenite, CHUKHROV (1950)—ehlite and (1951)—conichalcite, and RENGARTEN (1948)—goyazite.

9. *Sulphates*

Celestite was described by YARZHEMSKY (1948), brochantite and be udantite by CHUKHROV (1950a, b). The same author, (1950c) discussed the formation of jarosites, while SERDYUCHENKO (1951) described calcium jarosite. TZVETKOV and VALYASHIKHINA (1953) applied thermal methods to the study of alunites. YARZHEMSKY (1950) discussed the schönitization of langbeinite.

10. *Silicates*

A statistical study of the chemical constitution of potash-soda feldspars by BELYANKINA (1953) showed certain discrepancies between the actual data and the theoretical composition, but no explanation of this was arrived at. Other works on feldspars are on the coloration of amazonite by ELISEEV (1949) and on the calculation of the linear velocity of crystallization of plagioclases by LEONTIEVA (1949).

The formation of leucite from spodumene was discussed by PLYUSHCHEV

(1953). GINZBURG and KONONOV (1953) brough evidence to prove that caesium spodumen does not exist as a mineral species.

The following leucocratic silicates have been described; scapolite by BOBROVNIK (1948), pollucite by DYMKOV (1953), pectolite by SERDYUCHENKO (1949), chalcedony-like natrolite by KUZMENKO (1950), laumontite and analcime by RENGARTEN (1950), mordenite by BUSHINSKY (1950), stilbite, wellsite, thomsonite, prehnite, scolecite and heulandite, and zeolites in general by SHKABARA (1948a, b, c, 1949a, b, 1950).

The micas were studied by SERDYUCHENKO (1948a, b; 1951b, 1953), who proposed a scheme of classification of micas based on the relative proportions of R″ and R‴, postulating linear series phlogopite—biotite—lithionite—muscovite. Lithium-bearing micas were discussed by SHILIN (1953) and GINZBURG and BERKHIN (1953). The last two authors also discussed the phlogopite—biotite—lepidolite series and its relation to the talc—pyrophyllite—kaolinite series and the chlorite series. Soda-margarite was described by AFANASIEV and AYDYNYAN (1952).

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Various aspects of the chemistry of pyroxenes and amphiboles were discussed by BARABANOV (1948), KOSSOVSKAYA (1951), TZVETKOV (1948), LEBEDEV (1950; 1951), GINZBURG and GINZBURG (1950), GERASIMOV and others (1949) and VERBITZKY (1952).

Chemical composition, optical data and thermal properties of chlorites were discussed by IVANOVA (1949), GINZBURG (1953), SHABYNIN (1949), YANITZKY (1951), GORBUNOVA (1950), SERDYUCHENKO (1948) and SERDYUCHENKO and CHIRKOV (1951). SERDYUCHENKO (1953) also published a large memoir on chlorites, containing an extensive study of chlorites from the Northern Caucasus and other regions of the U.S.S.R. The descriptive part of this work is interwoven with a comparative study of world chlorites and this part of the work is supported by a large collection of chemical analyses, optical, X-ray and thermal data. The general scheme of classification is based on PAULING's structural formula for chlorites: $Y_mX_4O_{10}(OH)_8$, with $4 \leqslant m \leqslant 6$ and Y—cations in sixfold coordination (Al, Fe, Fe, Mg, Na, . . .) and X—cations in fourfold coordination (Si, Al, Fe).

Others silicates studies are—idocrase by CHUMAKOV and other (1948), AGAFONOVA and SVISTUNENKO (1949), ferrohortonolite by OVCHINNIKOV (1949), clinohumite by BORNEMAN-STARYNKEVICH and MYASNIKOV (1950), beryl by DORFMAN (1952), akhtarandite by LYAKHOVICH (1952), beta-cerolite by GINZBURG & RUKAVISHNIKOVA (1950), sepiolite by SERDYUCHENKO (1949), pumpellyite by KVASHA (1950), mangan-orthite by OVCHINNIKOV and TZIMBALENKO (1948), narsarsukite by BELYANKIN and VLODAVETZ (1949), lomonosovite by GERASIMOVSKY (1950), topaz and muscovite by POVARENNYKH (1950) and zircon by ZHIROV (1952).

(Clay and bauxitic minerals are discussed in Section V: Sedimentary rocks).

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III. MINERAL DEPOSITS

1. *Classification and Genesis*

MAGAKIAN's (1950; 1952) classification of ores is in harmony with the classification of rocks and his main divisions are (1) endogenetic, (2) exogenetic, and (3) metamorphic. Further subdivisions are according to compositional types and genetic setting. KROTOV (1953) and ZAKHAROV (1953) also adhere to genetic classification of economic deposits (metalliferous ores and non-metallic deposits). On the other hand, UKLONSKY (1953) insists on the classification of minerals and ores according to the leading elements. In this he is severely criticized by LEBEDEV (1950) and SAUKOV (1953). AFANASIEV (1950) makes an attempt to correlate the ores and igneous rocks of the Caucasus. TUROVSKY (1953) discusses postmagmatic ores, WOLFSON (1953) hydrothermal ores, and STRAKHOV (1953) hypergene ores.

BILIBIN (1951) criticizes the accepted zonal scheme of ore deposits and on the basis of newly observed facts of reverse zonality suggests that two types of zonality must be distinguished—depositional and pulsational. In a subsequent discussion KHRUSHCHOV (1953) brings additional evidence of reverse zonality, while KONSTANTINOV (1952), criticizing BILIBIN, argues that his depositional zonality is really identical with EMMONS' geothermal zonality.

Colloidal processes in ore formation and collomorph structures in ores are discussed by RADKEVICH (1952), CHERVYAKOVSKY (1952), LEVITZKY (1953) and GRIGORIEV (1953).

2. *Paragenesis of Minerals*

An elaborate mathematical physico-chemical study of mineral paragenesis in various environments and conditions, especially in the case of metasomatic processes, has been carried out by KORZHINSKY (1949a, b; 1950a, b, c; 1951a, b, c; 1952a, b; 1953a, b, c, d) and by NAKOVNIK (1949). A detailed and comprehensive study of the paragenesis of ore minerals, especially sulphides, also of the hydrothermal solutions and their role in the formation of vein deposits, has been published by BETEKHTIN (1949; 1950a, b; 1952; 1953a, b, c, d) and by BETEKHTIN and GENKIN (1951). All these papers are amply illustrated by

various types of diagrams and by photomicrographs of polished sections of ores. Among these sulphide and oxide ores get most attention than ores of hydrothermal origin and of colloidal origin. The scope and the depth of the work of KORZHINSKY and BETEKHTIN cannot be summarized briefly in a review article but there is no doubt that it is of paramount importance in the sciences of genetic mineralogy and ore deposits.

3. *Sulphide Ores*

OLSHANSKY (1948) discusses the importance of the factor of the fluidity of sulphide melts in the process of formation of sulphide ores, and he also gives an account of the quaternary system Fe—FeS—FeO—SiO_2 (1951). WEITZ (1952) discusses the metamorphism of melnikovite, pyrite and marcasite. PHILIMONOVA (1952) gives an account of the experiments of the heating of ores composed of pyrite and bornite and she suggests that chalcopyrite is a reaction product of these two minerals. ZAVARITZKY (1950) gives a summary of his extensive work, carried on over many years on the metasomatism and metamorphism of the Ural pyrite deposits. IVANOV (1950) and YAROSH (1953a, b) describe the internal structure of crystals of pyrite, especially their zonal structure, while KARASIK and others (1953) discuss the porosity of pyrite in relation to its paragenesis. KOROVYAKOV (1948) describes copper-nickel sulphides associated with the basic and ultrabasic igneous rocks in Siberia. KOZHUKHOV (1948) describes a new deposit of mercury in the Caucasus. SINITZIN (1948) and NEVSKY (1948) discuss the stratigraphic and tectonic environment of the mercury—antimony ores of Fergana in Central Asia.

3. *Hydrothermal and Metasomatic Ores*

Contact metasomatic (skarn) ores are discussed by GORZHEVSKY and KOZERENKO (1952), who describe also a new type of tin-iron skarn. The skarn ores are also discussed by KHISAMUTDINOV (1949), who describes phlogopite mica from a granite contact zone. Graphite deposits both in Siberia and Uzbekistan belong to the contact metasomatic type of deposits and these are treated by (1) SOLONENKO (1950) who describes the graphite deposits of Botogolsk district near Irkutsk, which were formed by the action of hydrous solutions along crush belts in syenite and limestone and (2) ABDULLAEV (1949) who describes graphite deposits from Uzbekistan, which occur along the contact zone of gabbro and limestone. RADKEVICH (1951) describes two types of tin ores: (1) associated with quartz and (2) associated with the sulphides and iron silicates, and he also discusses the probable genesis of these ore types. BARSUKOV (1953) finds that association of cassiterite with albitized rocks suggests that in the hydrothermal solution tin is transported in solution in the form of $Na_2(Sn(OH, F)_6)$ which, on hydration becomes $Sn(OH)_4$ and eventually SnO_2.

According to STEINBERG (1953) no sharp line of separation can be drawn between the magmatic and the contact metasomatic iron ores, the only difference being in the geological setting and a suggestion is made that true magmatic iron ores do not exist. ZAVARITZKY (1952) describes an unusual case of the probable metasomatism of a pisolitic iron ore into a magnetite vein in Siberia. According to POLOVINKINA (1949) sodium metasomatism is a regular phenomenon in the formation of ferruginous quartzites and jaspers. These types of ores are well represented in the Krivoi Rog ores deposits in the Ukraine, described and

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discussed by BELEVTZEV (1951; 1952), while the ferruginous quartzites of the Urals are described by SMIRNOV and SMIRNOVA (1948).

5. *Various Ore Deposits*

The paragenesis of oxides and hydroxides of iron in the pegmatites of Volynia is discussed by TZYGANOV (1951). The possible influence of carbonaceous shales on the precipitation of polymetallic ores of Altai is discussed by SERGIEV & TASHCHININA (1953) and the problems of the migration and of the structure of native gold are discussed by ALBOV (1952) and PERELYEV (1953). KHASIN (1949) gives an account of his field and chemical study of tungsten bearing veins, in which ferberite (Fe-wolframite) is predominant in the upper zone and hübnerite (Mn-wolframite) in the lower zone.

6. *Sedimentary Ores*

In a series of papers, KROTOV (1948; 1950a, b, c; 1951a, b, c; 1953) discusses various problems connected with the deposition of sedimentary ores of iron, manganese and aluminium in lakes and seas. He makes an attempt to find a relation between epirogenic movements, physico-chemical evironments, weathering-denudational processes and the types and facies of ore deposits. He also relates the precipitation of various iron, manganese and aluminium minerals to seasonal changes, and traces the processes of their subsequent metasomatic replacements and alterations. He also discusses the formation of ooliths and pisoliths and studies the distribution of oolithic iron ores in Europe. TOCHILIN (1951a, b; 1952) also discusses the formation of oolithic iron ores and the paragenesis of oxides and hydroxides of iron. He provides a detailed description of limonite, hydrogoethite, goethite, lepidocrocite, hydrohematite, and hematite and comes to the conclusion that turyite is a mixture of hydrogoethite and goethite. FORMOSOVA (1953) also discusses the formation of oolithic iron ores. POVARENNYKH (1952a, b) discusses the limonitization of the iron oxide minerals from the point of view of crystal chemistry. MIROPOLSKY and MIROPOLSKAYA (1948) discuss the formation of sphaerosiderite, while FLORENSKY and BALASHINA (1948) discuss the formation of siderite in the ancient crust of weathering. MAKHININ (1951) discusses the formation of glauconite in the Oligocene deposits of the Ukraine, while STRAKHOV (1950) gives a general outline of the formation of the sedimentary iron ores.

DRAGUNOV & KATCHENKOV (1953) describes bedded and concretionary deposits of celestite and barite found among shelly limestones and clays of the Upper Tertiary age, and they provide spectroscopic data for Na, Mg, Ca, Sr, Ba, Ti, V, Cr, Mn, Fe, Ni, Cu, Al, Si, Zr, and B in these rocks. On the basis of these data they discuss the genetic history of this deposit.

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Abbreviation:

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IV. IGNEOUS ROCKS

1. *General*

The veteran Russian petrologist D. S. BELYANKIN (1876–1953) summing up the present position in the science of igneous rocks (1951; 1953) is rather critical of the modern tendency to separate petrography (descriptive science) from petrology (interpretative science) because, in his opinion, interpretation without

description and description without interpretation are both meaningless. He also protests about the prevailing method of naming rocks after localities where they were first discovered. According to him rocks should be named according to their mineralogical composition and textural characters. He also protests against the exaggerated value placed on the recalculated chemical analyses of rocks and on the play with various coefficients and ratios. Y. A. KUZNETZOV (1951) and VERBITZKY (1952) also think that a rational nomenclature and a genetic classification of igneous rocks are most desirable. SOLOVIEV (1952) gives an account of the distribution of igneous rocks in the U.S.S.R. and at the same time discusses various problems connected with this distribution. ABDULLAEV (1950) emphasizes the importance of the country rocks as a source of material assimilated by the magma leading to hybridism and even differentiation. The rôle played by the volatiles in the magma and the possible magmatic liquation as a cause of differentiation, all these questions are the subjects of a vigorous discussion. SHIPULIN (1953), for example, brings forward the evidence of the presence of gas-liquid inclusions in the minerals of granite as a definite evidence of the abundance of volatiles in the magma. On the other hand BELYANKIN (1949) in discussing the arguments in favour of magmatic liquation, as brought forward by LOEWINSON-LESSING and FENNER, is still reluctant to accept the available field and petrographic evidence as wholly valid, and he suggests that more work has to be done as yet in the field of the experimental study of the silicate-water system, and this is precisely the theme of the controversy between OSTROVSKY (1950; 1951; 1952a, b) and NIKOLAEV (1951; 1952; 1953a, b) who deal with the mathematical-theoretical side of liquation, immiscibility and the formation of hydrothermal solutions.

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2. *Granites*

Like everywhere else the granite controversy is affecting the peace of Russian petrologists. A special meeting held in Moscow on April 3rd to 10th 1953, was devoted to the problems of magmatism and the relation of magmatism to the formation of ore deposits. At this conference 680 members from thirty-one towns were present and thirty-one papers were read. The conference as a whole did not approve the extreme tranformist view, but it did not exclude the possibility of a deep-seated metasomatism and of the assimilation of crustal rocks by the magma, leading to hybridism and differentiation.

The extreme transformist view is represented by SUDOVNIKOV (1950) who postulates nearly all granites as being formed through metasomatism of the country rocks, but makes a provision for magmatic granites as the last stage of progressive metasomatism. Other petrologists, without accepting this extreme view, adduce evidence for the metasomatic origin of certain igneous rocks. Thus for example, KATKOVA (1949) in her work of the granites of Tian-Shan, finds a widespread late-stage microclinization, suggesting potassium metasomatism, or rather autometasomatism of a magmatic granite. FLORENSKY and LAPIDSKAYA (1953) also describe microclinized granites. Gaseous emanations as the cause of recrystallization of granite are invoked by DMITRIEVSKY (1952) in explanation of the peculiar textural features of granites in Kazakhstan. POLKVOY (1952) suggests intensive action of magmatic emanations to explain the formation of granites out of acid lavas, limestones and sandstones. LYAKHOVICH (1952) describes granitization of hornfelsed xenoliths of country rocks. AFANASIEV

(1949a, b; 1951; 1952; 1953), in a series of articles dealing mainly with the Caucasian granites, discusses the origin of granites and igneous rocks in general. He accepts the evidence of an endomorphic microclinization of granites by volatiles, but he also emphasizes the magmatic origin of the majority of the granites. Granitic magma or any other kind of magma, according to him, represents a product of remelt of a portion of the earth's crust. These magmas, rich in volatiles, are the sole sources of granitizing emanations. Thus granites may be of pure magmatic or of pure metasomatic origin. Y. A. KUZNETZOV (1953) also agrees that it is futile to postulate a monogenetic or universal hypothesis—granites may have a different genetic history—magmatic or metasomatic, fusive or assimilative. KROPOTKIN (1953) also provides an important contribution to this discussion by marshalling data relating to the cosmological stage of the earth's evolution. KORZHINSKY (1952) considers that the constant polymineralic composition of granite excludes the possibility of a purely metasomatic origin and suggests instead infiltration of magmatic solutions. NIKOLAEV (1953) discusses the problem of genesis of granite from the physicochemical point of view. ELISEEV (1951) strongly opposes the extreme transformist hypothesis. KUPLETSKY and CHUMAKOV (1948) postulate a magmatic origin of the granites of Kola peninsula. ZARIDZE (1952), on the basis of the study of igneous rocks of Georgia, comes to the conclusion that magmatic rocks cannot and must not be studied in isolation from the general background of tectonism and geological history of the district in which they occur. FROLOVA (1953) from her field study of Siberian granites comes to the conclusion that in this particular district concordant granites are of ultrametamorphic origin, while discordant granites are of magmatic origin. E. A. KUZNETZOV and ZINOVKIN (1953) also find strong evidence for the presence of these two types of granites in the Urals.

Purely descriptive works on granites and other acid igneous rocks are as follows: POVARENNYKH (1951) describes granite-limestone contact skarn containing mushketovite (pseudomorph of magnetite after hematite). DMITRIEVSKY (1952) describes various types of greisen from Kazakhstan, KROTOV (1952) describes biotite granite from northern Caucasus. GRUSHKIN (1952) and SIDORENKO (1952) describe alterations of granodiorite in the vicinity of mineral veins, BUTAKOVA (1950) describes granite-syenite complex from the Alai range, SALOP (1949) describes pseudotachylyte from the Baikal region and outlines the genetic series: pseudotachylyte—cataclasite—tectonic breccia.

3. *Pegmatites*

Pegmatites, products of crystallization of volatile-enriched residual magma, as well as aplites and mineral veins, are the subjects of ZAVARITZKY's (1944; 1950; 1953) general surveys and theoretical discussions. A detailed study of the facies of pegmatites and of the phases of their genesis is done by VLASOV (1946; 1951; 1952a, b), with a particular attention paid to the mineral associations in the zones of the pegmatite veins corresponding to the successive genetic phases. The zonality of pegmatites is also discussed by BEUS (1948; 1951) and ADAMIAN (1949). Strontium in pegmatite minerals, such as barytocelestite, zoisite, apatite and others, is discussed by AFANASIEV (1948). Contrasted view on the genesis of pegmatites are presented by V. I. KUZNETZOV (1951), who is of the opinion that the process of pegmatite formation begins at the very beginning of the crystallization of magma, and by NIKITIN (1950), who by contrast, from his study of

Karaelian mica pegmatites, comes to the conclusion that these pegmatites were not formed from a melt, but through a lengthy processes of transformation and segregation metasomatism and hydration, in the solid body of the granite itself.

4. *Basic and Ultrabasic Plutonites*

MORKOVKINA and LUPANOVA (1953) describe banded gabbro-amphibolites of northern Urals which, in their opinion, are not the products of differentiation of a basic magma, but are the products of injection-metasomatism of the plagiogranite magma acting on the ultrabasic and sedimentary country rocks. On the other hand YAKOVLEVA (1948) postulates magmatic differentiation as the cause of the variable composition of the gabbro-diabase intrusive masses of Taimyr peninsula, in which the lower parts of the sills are enriched in olivine. VERBITZKY (1951) describes micropegmatite intergrowths in quartz diabase in the Ukraine.

Ultrabasic rocks from the Caucasus are described by SERDYUCHENKO (1949), LEONTIEV and KHAIN (1949) and SOBOLEV (1953), from Fergana—by LEBEDEV and VAKHRUSHEV (1953). In the last work a new rock name "ferganite" is applied to a variety of micropyroxenite. A general discussion on the origin and significance of ultrabasic rocks is provided by EGOYAN and KHAIN (1953).

5. *Rocks of Volcanic Association*

KROTOV (1952) describes trachyliparites from northern Caucasus which are assumed to have been produced from an anchieutectic magma which has crystallized in two stages—phenocrysts and groundmass, both of the same or nearly the same chemical composition. SOLOVKIN (1948) describes quartz porphyries from Transcaucasia, and SOLOVIOV (1950) describes acid effusive rocks and ignimbrites from Sikhote-Alin range in eastern Siberia. The study of the minerals of the lamprophyres leads SOBOLEV (1952) to the conclusion, that lamprophyres were formed through the assimilation of granite by a basic magma.

A large number of petrographical works deal with the rocks of Central Asia, Mongolia, Siberia and Kamchatka. GONSHAKOVA (1953) describes effusive basic to acid rocks of Pre-Cambrian and Palaeozoic ages from Chingiz range in Central Kazakhstan. GAPEEVA (1949; 1951; 1952) describes camptonites, bekinkinites and basalts from Toyun, southern Tian-Shan. LEBEDEV and GINZBURG (1953) describe Lower Palaeozoic basic-acid rocks of Tuva (southern Siberia). VLODAVETZ (1950; 1952) describes volcanoes and their lavas from Darigan region in Mongolia, and a new variety of calcite-diabase, which he names "cabytauite", from southern Mongolia. The calcite in this rock is fresh and it is assumed that it is of magmatic or epimagmatic origin. Various aspects of "Siberian traps" are noted by GONSHAKOVA (1951; 1953) and KOROVYAKOV (1948). New discoveries of volcanoes of Tertiary and Quaternary ages are made in northern and eastern Siberia. VASKOVSKY (1949), for example, describes a well preserved volcanic cone composed of a highly vesicular glassy basalt situated in the basin of the river Indigirka in north-eastern Siberia. MALEEV (1949) describes six volcanic cones of Quaternary age situated along a tectonic line stretching from Vladivostok to Nikolaevsk. In Kamchatka, MENYAILOV (1949) described Kharchinsky and Zarechny volcanoes and their basaltic lava flows, while NABOKO (1953) describes the sublimates and efflorescences of Shiveluch volcano, and BASHARINA (1953) describes gases from fumarola, lavas and agglomerates-flows of Klyuchevsky and Shiveluch volcanoes.

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V. SEDIMENTARY ROCKS

1. *General*

Works dealing with the genesis and classification of sedimentary rocks are very numerous. Text-books by PUSTOVALOV (1940), SHVETZOV (1948) and STRAKHOV (1948) provide useful summaries of the science of sedimentary rocks in its various aspects.

2. *Genetic Aspect*

The genetic aspect of sedimentary rocks was a subject of numerous debates during the last decade, culminating in a conference on sedimentary rocks and sedimentary ores held in Moscow in November 17th to 24th 1952 in which 1077 participants from sixty-three towns were present and sixty-seven persons took part in discussions. Prior to this a large volume containing some twenty articles was published (PUSTOVALOV, STRAKHOV and others, 1951). During the conference, debates, often heated, centred on two contrasted hypotheses regarding the mechanism of the process of formation of sedimentary rocks—that of STRAKHOV and that of PUSTOVALOV. STRAKHOV (1949; 1950a, b; 1951; 1952; 1953) presents a very broad picture of sedimentary rock formation, a picture based on an extensive data and relating to weathering and sedimentation in all their chemical and mechanical aspects. His main thesis is that of HUTTON's

that the present is the key to the past, and that the knowledge of modern processes of sedimentation can be applied to the study of ancient sediments. The main criticism of STRAKHOV by PUSTOVALOV (1950; 1951) is that the principle of actualism cannot be rigidly applied in science of geology, for the external conditions and environment cannot be assumed to remain constant through the ages. Other aspects of genetic sedimentology are discussed by KROTOV (1949; 1952), SAPOZHNIKOV (1950), MURZAEV (1950), SOKOLOV (1953), SIDORENKO (1952) and VISHNYAKOV (1953).

3. *Weathering*

The soil studies inaugurated by DOKUCHAEV and GLINKA led to a considerable attention being paid to the study of the processes of weathering. Excellent exposition of the modern geochemical approach to the science of weathering can be found in the works of POLYNOV (1933; 1934; 1937). Recently an important work on the ancient crust of weathering of the Ural Mountains was published by GINZBURG and RUKAVINSHNIKOVA (1951). In this work a large number of minerals belonging to the zone of weathering are studied by various methods —chemical, thermal and X-ray. Purely geochemical aspects of weathering are discussed by LOPATIN (1950) who calculates the amount of chemical denudation of the earth, especially the amount removed in solution. MAXIMOVICH (1953) extends LOPATIN's work and studies chemical denudation of the continents. KROTOV (1953) provides a general survey of the differential mobilities of the elements and of their distribution among the sedimentary rocks.

4. *Clays and Clay Minerals*

Argillaceous sedimentary rocks are described by AVDUSIN (1953). SEDLETZKY (1945; 1951; 1952; 1953), SEDLETZKY and DZHUMAILO (1953) and SEDLETZKY and SAMODUROV (1950) describe the fine fractions of clays composed mainly of colloidal-disperse minerals. Methods of study of clay minerals are discussed by GORBUNOV and SHURYGINA (1949), GORBUNOV, TZYURUPA and others (1952), VEDENEEVA and RATEEV (1952), MIESSEROV (1953), PETROV (1948), KATCHENKOV (1949), SERDYUCHENKO (1949) and DILAKTORSKY and ARKHANGELSKAYA (1953).

Kaolinite clays and kaolinite minerals are described by LEBEDEV (1953) who redetermined the thermal effects of kaolinite. SEDLETZKY (1949) studied monothermite, a variety of kaolinite. Momothermite has been discovered in various clays and in various localities by SEDLETZKY (1949), SEDLETZKY and SAMODUROV (1949) and BEZBORODKO and MAZO (1951).

Donbassites, a group of clay minerals intermediate between kaolinites and chlorites, are described by LAZARENKO (1950; 1952).

Halloysite, metahalloysite and the like, are described by SAMODUROV and SEDLETZKY (1948a, b), chrome-halloysite is described by GRITZAENKO and GRUM-GRZHIMAILO (1949), ferrihalloysite is described by VAKHRUSHEV (1949).

Montmorillonite group of clay minerals is described by ZVYAGIN and PINSKER (1949) and by ZVYAGIN (1952), who have studied them by the method of electron diffraction. Montmorillonite clays are described by KUADZHE (1953), KIRSANOV (1948), ALESHIN (1948), ZVYAGIN, LAPIDUS and PETROV (1949). The last authors describe varieties of montmorillonite clays from the Caucasus named askanglina and askangel, later described in detail by BELYANKIN and PETROV (1950). YUSOPOVA (1950) discusses the formation of montmorillonite. CHUKHROV and ANOSOV

(1950) and SEDLETZKY (1950) describe medmontite—a copper montmorillonite. SEDLETSKY (1951) also describes magnymontmorillonite, a new variety of magnesium rich montmorillonite. BOBROVNIK (1951) describes a bleaching clay of fuller's earth type similar to askanite.

Finally ENTZOV, IGNATIEV and STARKOV (1952) describe volkonskoite—a chrome-bearing clay, and CHUKHROV and ANOSOV (1950) describe chrysocolla.

5. *Bauxites and Bauxitic Minerals*

BENESLAVSKY (1951a, b; 1952; 1953a, b) discussing the environment under which bauxites have been formed, suggests that the optimum environment is that of reducing conditions and the evidence for this is the presence in bauxites of minerals typifying such conditions, such as iron sulphides and iron carbonates. According to BENESLAVSKY pyritic facies are associated with monohydrate bauxites, while siderite facies are associated with trihydrate bauxites. Later hypergene conditions producing oxidizing reactions are apt to mask the original composition of bauxites. The structure of bauxites is distinctly of colloidal origin. Kaolinite, quartz and titanium minerals present in mature bauxites are not of primary terrigenous origin but represent minerals recrystallized from gels. Boehmite in bauxites is present in a crysptocrystalline state both in monohydrate and trihydrate types of bauxite.

VISHNYAKOV (1953) outlines the three genetic stages in the process of bauxite formation: (1) early stage of diagenesis during which alumogel is transformed it into alumometastabilite, (2) late stage of diagenesis, characterized by dehydration, during which hydrargillite is transformed into boehmite, (3) stage of metamorphism, during which diaspore is transformed into corundum.

GLADKOVSKY and SHAROVA (1953) in their study of the Asiatic bauxites of Cretaceous age, discuss the formation of pisolithic bauxites, which they consider to be of secondary origin and a product of redeposition of primary laterite. A comparative study of the chemical composition of the pisoliths and of the matrix show that pisoliths are richer in alumina and silica.

6. *Limestones*

A large-scale study of carbonate rocks of Russia and their distribution in time and space is made by RONOV (1948) and VINOGRADOV, RONOV and RATYNSKY (1952). This work represents a continuation of a planned investigation which began some ten years ago. It is based on a statistical estimation of volumes of various sedimentary rocks of different geological periods over the area of European Russia, combined with the study of their average chemical composition. It is concluded that each sedimentary cycle begins with an intensive deposition of fragmental rocks at the expense of chemical and organogenic precipitates, and that among the calcareous rocks the amount of Ca and Sr are increasing with the ago of the sediments, while the amount of Mg is decreasing.

Among other papers dealing with limestones are—SHAMRAY (1949) who describes microspherulitic limestones containing coccoliths of organic origin, TATARSKY (1949) who discusses dedolomitization of dolomites, APRODOVA (1949) who presents a statistical study of porosity, in amount of insoluble residue and chemical composition of limestones of Carboniferous age of Perm province, BANKOVSKY (1950) who discusses the chemistry and the lithology of the Carboniferous limestone of DONETZ basin and YURKEVICH (1953) who finds

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that the composition of the insoluble residue of limestones may serve as an indicator of facies.

7. *Phosphates*

A popular book on phosphates is published by BUSHINSKY (1952). The formation of phosphate deposits in relation to geotectonics is discussed by KAZAKOV (1950), who notes rhythms of phosphorite deposition during the Mesozoic era in Russia and compares these deposits to the phosphorite deposits of Permian age of the U.S.A. Late Cretaceous—early Eocene phosphorites of the Urals are described by RENGARTEN (1948). Phosphate phytomorphs from the brown iron ore are described by FORMOSOVA (1952), who also discusses the chemistry of replacement of fossil wood by phosphates.

8. *Silica Deposits*

VOTINTZEV (1948) gives an account of the geochemical rôle of sponges in the silica cycle of the Lake Baikal. POPOV (1951) describes copper-bearing sandstones of hydrothermal origin of central Kazakhstan. SIDORENKO (1953) describes the formation of silicified cement and silica concretions of Turkmenistan as examples of desert silicification. BRUEVICH (1953) finds that in the sea water silica is present mainly in the form of monomolecular solution of H_2SiO_3 and in proportions well below the saturation value. This suggests the only possible form of precipitation that of biochemical nature. VISHNYAKOV (1953) describes silicified limestone, chert nodules and geodes, all composed mainly of chalcedony, with small amount of quartz and opal, and formed through replacement of limestone or pore infilling.

9. *Elements in Sedimentary Rocks*

The distribution of occurrence of sundry elements in sedimentary rocks are the subject of the following works: ITKINA (1948) on Cu in Carboniferous rocks of Urals-Volga region, VINOGRADOV and VINOGRADOVA (1948) on Mo in soils of the U.S.S.R., GULYAEVA (1951a, b) on I and in Devonian rocks of Urals-Volga region, GULYAEVA (1953) on C, S and Fe in Devonian and Carboniferous rocks, ZALMANZON and SHISHOVA (1952) on Fe, Mn, P, and other elements in Devonian rocks of Volga region, KAVEEV (1953) on N in Carboniferous and Permian rocks of Tartar region, and finally, KATCHENKOV (1951; 1952) on the elements and the correlation by means of elements of Permian rocks of Volga-Kama region, a work based on the spectrographic determination of elements.

10. *Biosphere in General*

The distribution and concentration of elements in plants, fossil coal and petroleum are discussed by VINOGRADOV (1952) and KATCHENKOV (1952). Among numerous papers published in various scientific and technical journals on the chemistry of coals and bitumens we have the paper of KARTZEV (1949) on the selective extraction—luminiscence method of soluble fractions by means of five different solvents from coals and bitumens. The results of these extractions are plotted as characteristic diagrams which can be used for the identification of various grades of coals and bitumens. The redox potential of caustobiolites is studied by GULYAEVA and ITKINA (1951). The formation of organo-mineral compounds among clays, is studied by KHAN (1951). A regional study of

biogeochemical provinces of sourthern Urals, based mainly on the records for the amounts of Co, Ni and Cu in soils, ground waters and ash in plants and animals is carried out by MALYUGA (1950). The geochemical activity of bacteria is tested by an experimental study by KALINENKO (1952) on the precipitation of calcareous and ferruginous colloidal gels. The nature of mud volcanoes associated with petroleum bearing strata, and geochemistry of gases derived from mud volcanoes are discussed by RONOV (1949; 1951).

11. *Coals*

Books by ZHEMCHUZHNIKOV (1948) and PORFIRIEV (1948) deal with coals in general. Regional studies of coals, having bearing on their composition, are by MATVEEV (1950), who discusses the influence of geological factors on the nature of coals, by KRASHENINNIKOV (1950), who discusses the connection between the geological setting and the character of coal-material assimulation, and by ZHEMCHUZHNIKOV (1952), who discusses the South Wales coal basin as an example of a region with a markedly zonal distribution of coals of various ranks. This enables him to reconstruct the tectonic history of the region.

The microscopical study of coals as a clue to their genetic history is discussed by AMMOSOV (1952), who among other thing, proposes a new term "desmite" for the amorphous groundmass of bituminous coals. The refractivity of desmite is studied by AMMOSOV and MUSYAL (1952), who find that there is a regular increase of refractivity as we advance from brown coal towards anthracite. On the basis of this they postulate eight stages of metamorphism of coal. On the other hand, KRYLOVA (1952) uses refractive index of coal as the criterion of metamorphism and she even proposes a formula connecting up the refractive index (N) with the amount of volatiles in coal (V), namely $V = 315{\cdot}5 - 150\,N$. GINZBURG (1951) gives a petrographical classification of bituminous coals. KASATOCHKIN, ZOLOTOVRATSKAYA and RAZUMOVA (1951), on the basis of X-ray study, trace the transformation of the fine structure of coals during the different stages of their metamorphism. KASATOCHKIN (1952) continues this work and concludes that vitrain is a "space polymere" or "polycondensate" of irregular structure made of macromolecular layers, each molecule having side chains. The metamorphism of coal, according to him, consists in the growth and reorientation of the macromolecules. KASATOCHKIN and RAZUMOVA (1953), on the basis of thermal treatment of coal, study the degree of order-disorder and the growth of carbon layers molecules. The relation between the stages of metamorphism of coal and the absorbent properties of coal are traced by KHODOT, ETTINGER and YANOVSKAYA (1953). Sapropelic coals are described by LARISHCHEV (1948), who suggest new names—"psylophylitic liptobiolite" and "barsasite" for varieties of sapropelic coals from Barsas, Kusnetzk basin. The application of luminescence method to the study of sapropelic coals is made by AMMOSOV and ERMAKOVA (1950). The study of humic acids extracted from peats and coals is made by KASATOCHKIN and others (1950), KUKHARENKO and others (1952), KUKHARENKO (1949) and KUKHARENKO and SAVELIEV (1952) and KLIMOV and others (1953).

12. *Bitumens*

A genetic classification of bitumens is outlined by USPENSKY and RADCHENKO (1952). A detailed study of the amounts and composition of hydrocarbons

contained in various sedimentary rocks is given by USPENSKY, CHERNYSHEVA and MANDRYKINA (1949). The study of organic matter contained in sedimentary rocks by the luminescence method is undertaken by KARTZEV (1949), while DATZKO (1948) gives a detailed account of the soluble organic matter in sea water, and its accumulation in sedimentary rocks. TAGEEVA (1951) studies geochemical factors of formation of petroleum in sedimentary rocks. Mention should also be made of an earlier paper by BATURIN (1945) on the origin of petroleum. Geochemical indicators of petroleum are discussed by KOVDA, SLAVIN and others (1951).

The elemental composition of petroleum ash is discussed by KATCHENKOV (1948; 1949a, b; 1951) Spectroscopic study of petroleum and associated sedimentary rocks is done by KHMELEVSKAYA and others (1948). Hydrochemical and thermal indicators of petroleum are discussed by SUKHAREV (1951), boron-chlorine coefficient of oil-waters—by KAZMINA (1951), hydrochemical methods of oil prospecting—by KAVEEV (1948), the connection between asphalts and petroleum—by RADCHENKO and BOLOTSKAYA (1949), the study of bitumens by means of infrared light spectra—by GLEBOVSKAYA and ZAKHAROV (1953), and the criteria for the autigenous or allothigenous origin of disperse bitumens—by MEKHTIEV and DIGUROVA (1953).

Sundry natural hydrocarbons described are curtisite ($C_{24}H_{18}$) from Transcarpatia described by FRANK-KAMENETZKY and MALEEVA (1953) and a new substance named evenkite ($C_{21}H_{42}$) from Evenki, Siberia described by SKROPYSHEV (1953).

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VI. NATURAL WATERS AND EVAPORATES

1. *General*

The study of natural waters—ground waters, mineral waters, river, lake and sea waters—has a long standing tradition in Russia, but during the last three decades this branch of research has been developed on a very large scale. VERNADSKY was very interested in the study of natural waters as an integral part of regional geochemistry and in 1933 (VERNADSKY, 1933) he published a most elaborate classification of natural waters into groups, sub-groups, classes, subclasses and

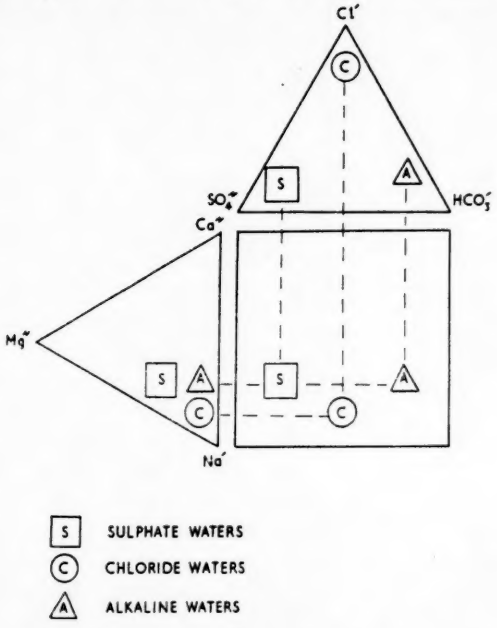

Fig. 1. Diagram showing the composition of natural waters. %mg/equivalents: anions 100, cations 100, plotted on the anion and cation triangles and projected on the "salt square." Each analysis is thus represented by means of three points. (DUROV, S. A. (1948) *C.R. (Doklady) Acad. Sci. U.S.S.R.* **59**, 87.)

species, of which he enumerated 485 in all. At the present time the study of natural waters is spread over a great number of sciences, such as hydrogeology, geochemistry, the science of petroleum, the science of evaporates, limnology, oceanography, balneology, hydrobiology, and others. The number of books and papers dealing with all these aspects is very large. A very small selection of books include those of ALEKIN (1948; 1953), OVCHINNIKOV (1947), SULIN (1935; 1946; 1948a, b) and RODE (1952).

Different types of graphical representation of the chemical composition of waters are used at the present time in Russia. FILATOV (1948), for example gives a description of a square, rhombic, and circular diagram. DUROV (1948) is using a square in combination with two triangles (Fig. 1), which is really a modification of the diagram proposed by G. S. ROGERS in 1917. To use this diagram cations and anions must be added up to 100 and plotted separately on

the two triangles. The intersection of the two perpendiculars from these two points to the sides of the square give a point in the "salt square". On the basis of this diagram DUROV distinguishes eighteen types of natural waters made of the six ions: Mg, Ca, Na, HCO_3, SO_4 and Cl.

Another type of diagram is used by SPIRO, GRAMBERG and VOVK (1953). This diagram (Fig. 2) is based on the contents of the most soluble salts in the water and it also consists of a square and two triangles, but in a different combination as compared with DUROV's diagram. Apparently this diagram was first used by O. D. KOSHKAROV in 1938. As represented in Fig. 2 this diagram shows the fields of typical waters—rivers, lakes, seas and oilfield waters.

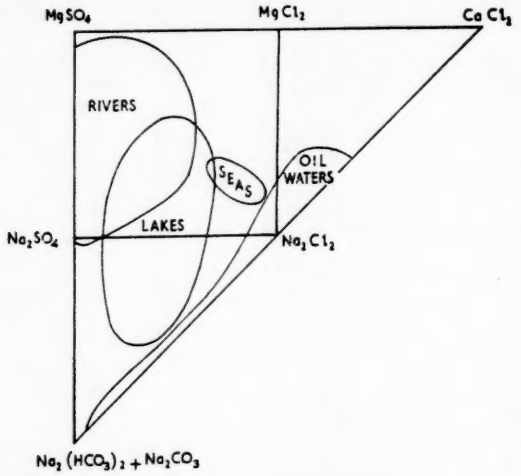

Fig. 2. Diagram showing the composition of natural waters. One point represents each analysis recalculated to $Na_2(HCO_3—CO_3)—CaCl_2—MgSO_4$ 100. Four distribution areas are shown: river waters, lake waters, sea waters and oil waters. (SPIRO, N. S., GRAMBERG, I. S. and VOVK, Z. L. (1953) *C.R. (Doklady) Acad. Sci. U.S.S.R.* **93**, 532.)

2. *Ground Waters*

The proposed schemes of classification of ground waters show great variation, and this variation primarily depends on the regional characters. Thus, for the oilfield waters of Saratov district, FEIGELSON (1948) proposed a two-fold classification: (1) sulphate-sodium and bicarbonate-sodium, and (2) calcium chloride brines. On the other hand ground waters are classified by SHAGOYANTZ (1948) into (1) bicarbonate-calcium, (2) sulphate-sodium, (3) bicarbonate-sodium (alkaline), (4) chloride-bicarbonate-sodium, and (5) chloride-sodium. According to MAKARENKO (1950) carbonate alkaline waters are of hybrid origin. Even more complex origin of chloride-alkaline-calcium waters is postulated by SAIDAKOVSKY and others (1951) and of sulphate waters—by KUDRIN (1953). Hydrochemical facies of ground waters of the Tartar region are discussed by SELIVANOVSKY and others (1949). Horizontal and vertical zonality of ground waters are discussed by MARINOV (1948a, b), SILIN-BEKCHURIN (1951; 1952), GORBOV (1951), DUROV (1951) and DUROV and GORBENKO (1953). Dolomitization of rocks caused by

ground waters is discussed by AFANASIEV (1948), ore formation due to the same agency—by GERMANOV (1953).

Several works are devoted to the study of chemical elements in ground waters. Thus, VINOGRADOV (1948) gives an account of the disperse elements in ground waters and discusses the significance of the coefficient of proportionality for certain couples of elements, such as Ca/Sr, Ra/Ba, K/Rb and Cl/Br. DODONOV and others (1949) discuss the occurrence of alkaline earth metals. The determination of iron in ground waters is described by SHIKLOVSKAYA-OVCHINNIKOVA (1953), and of organic carbon—by SKOPINTZEV (1948) and by DATZKO and DATZKO (1950).

3. *River Waters*

The part played by rain and snow on the composition of river water is discussed by MAXIMOVICH (1953), while DUROV (1951; 1952) discusses the possible sources of salts which are dissolved in river water. FORSH (1949) calculates formulae applicable to the calculation of the concentration of ions as a function of the rate of flow. PONAMAREVA and ETTINGER (1953) discuss the nature of organic matter present in river water, while GROMOVA (1953) discusses the mineralogical composition of the delta deposits of the river Don.

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4. *Lakes in General*

VINBERG & ZAKHARENKO (1950) discuss the part played by the plankton in the carbon cycle in lakes. VOTINTZEV (1950, 1953) studies biogenic elements in the water and in the water of the lake Baikal and in the water contained in the bottom sediments of this lake, while RATEEV (1952) studies the clay minerals of these sediments. ROZEN (1951) studies the absorption of iodine and bromine by the bottom sediments in lakes, SAVINOV and others (1950) studies the distribution of carotine in the medicinal muds of Ukrainian lakes, and DUROV (1950) discusses the accumulation of sulphates in waters of ponds of Salsky steppe, and KUZNETZOV (1949; 1952) studies the microbiology of lake oozes.

5. *Salt Lakes and Brines*

LEPESHKOV and BODALEVA (1952) discuss the order of crystallization of salts during evaporation in the large bay of Kara-Bogaz-Gol and on the content of salt in the Caspian Sea. DODONOV and others (1948) gives the results of the experimental fractional crystallization of salts from brines. NIKOLSKAYA (1951) discusses salt formation in salt lakes of Kulundzha. KLOCHKO (1950) provides certain theoretical formulae and coefficients relating to the change of salinity in lakes. EPSTEIN and ANFEROVA (1950; 1952) discuss the periodic cycles of salt deposition in the lakes of Barabinskaya steppe, and also the problem of the ionic exchange between the bottom deposits and the brine. POSOKHOV (1949) describes calcium chloride lakes of Kazakhstan. VITAL (1951) gives the results of his study of mirabilite and colloidal carbonates and hydrates of magnesium in the waters of lake Elton. GORBOV (1950) discusses the genesis of thenardite in the lakes of Kulundin steppe and its relation to mirabilite and halite.

6. *Evaporates*

LOBANOVA (1953) discusses the formation of langbeinite found among the Subcarpatian potash salts deposits and the paragenesis of langbeinite-halite and

langbeinite-kyanite polymineralic rocks. VALYASHKO and NECHAEVA (1952) give the results of their experimental study of the formation of polyhalite. FEDOTIEV (1949) provides a geochemical diagram of evaporates. YARZHEMSKY (1949) discusses petrographical characters of modern evaporates mainly those of the lake Elton. V. I. SCHERBINA (1948; 1950) and V. N. SCHERBINA (1949; 1952) and BERGMAN and SHCHERBINA (1950) describe the Tertiary salt province of northern Tian-Shan and Kirgizia and discuss the formation of halite, glauberite, mirabilite, thenardite, halite and gypsum. BUDNIKOV and MCHEDLOV-PETROSYAN (1948) discuss the formation of a natural mixture of gypsum and clay, called locally "gazha", a substance accumulating in the subsoil of the dry climatic regions of Caucasus and other regions of the U.S.S.R.

Several works deal with the Solikamsk potash salts deposits discovered in the district of Perm in 1926 mainly through the effort of N. S. KURNAKOV. Since that time these deposits have been systematically surveyed and extensively worked. The latest works dealing with the Solikamsk evaporates are one by FIVEG (1948), who discusses the annual cycle of deposition of halite, by VALYASHKO (1951) on the process of crystallization of sea salts and its bearing on the process of formation of Solikamsk deposits, and by DUBININA (1951) on the genesis of sylvine in these deposits.

Inder borate salts deposits in western Kazakhstan, discovered in 1934, first as typical lake deposits, but later as salts in the cap rock of a underlying salt dome of Permian age. The latest works dealing with Inder borates and other associated salts, are by YARZHEMSKY (1949; 1952; 1953a, b) who describes polyhalite, kurgantaite (a new borate mineral), hydroboracite, and other minerals. SPIRYAGINA (1949) discusses the conditions of formation of kurnakovite and NIKOLAEV (1947) discusses physico-chemical aspects of natural borates and the genetic history of Inder borates.

7. *Seas*

General account of the geology and geochemistry of the seas are contained in the books by KLENOVA (1948; 1949). SELIVANOV (1947) discusses the origin of chlorine and bromine in the ocean water and suggests that the annual output of chlorine from the world's volcanoes which is the order of 10^6 to 10^7 tons per annum is sufficient to provide the total amount of chlorine in ocean water which, according to F. W. CLARKE is $2{\cdot}72 \times 10^{16}$ tons accumulated during $n \times 10^9$ years. Bromine is probably derived from the same source. GULYAEVA (1948) discusses the content of boron in marine oozes and provides data for various types of oozes in different seas. OSTROUMOV and SILINA (1952) study the distribution of vanadium in the bottom deposits of Okhotsk Sea and they find that vanadium is more abundant in deposits adjoining volcanic islands and they suggest therefore, that vanadium is primarily derived from igneous rocks. KLENOVA and GERSHANOVICH (1953) give an account of the geochemistry of the deep sea deposits of the Sea of Japan. TEODOROVICH (1949) discusses siderite facies of sea deposits and their connection with the oil bearing strata.

The Black Sea is still the favourite hunting ground for Russian biogeochemists with its lower hydrogen sulphide foetid zone and the black bottom mud. GOLOLUBOV and PIROGOVA (1948) discuss the position of the upper surface of this zone which on the average 170 m below the sea level. The hydrogen sulphide in this zone is assumed by them to be formed in two stages: (1) $MeSO_4 + C_2$

$= MeS + 2CO_2$, (2) $MeS + CO_2 + H_2O = MeCO_3 + H_2S$, Me standing for Ca, Mg, etc. The following five papers are dealing with the amounts and the distribution of the biomass in the various zones of the Black Sea: KRISS, RUKINA and TIKHONENKO (1950) are mainly concerned with the rich bacterial biomass of the hydrogene sulphide zone, MOROZOVA-VODYANITZKAYA (1950) discusses phytoplankton of the upper zone, DATZKO (1951) discusses the amounts of organic carbon in the different levels of the sea, KRISS, LEBEDEVA and RUKINA (1952) discuss the distribution of the biomass along a horizontal traverse, and KRISS and LEBEDEVA (1953) discuss the distribution of the biomass of the upper zone of the Black Sea.

GOLOLOBOV (1949) discusses the geochemical balance of Si and P, variations of salinity and other factors as bearing on the age of the modern phase of the Black Sea. The bottom deposits of the Black Sea are studied by RATEEV (1952) who gives an account of the clay minerals present in them, MALYUGA (1949), who studies the amounts of Co, Ni and Cu present in them, and OSTROUMOV (1953) who studies the distributions of the rare earths in the bottom deposits which he finds concentrated in the colloidal fraction. The amount of organic matter in the Black and Azov Seas, as determined by the oxidizing capacity of the water is calculated by SKOPINTZEV (1952).

Papers relating to the Azov Sea are those by FEDOSOV (1952) who studies the amount of sedimentation, DATZKO (1948) on the deposition of phosphates among the bottom sediments, GORSHKOVA (1952) on the nature of organic matter in the bottom sediments SAVICH (1950) and ROMM (1950) on the Taman peninsula.

The Caspian Sea is studied by BRUEVICH (1941) and more recently by BRODSKAYA (1949). The Aral Sea is studied by RATEEV (1952) who described clay minerals in the bottom sediments.

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